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REGULAR ARTICLE

Equidensity orbitals in *resultant*-information description of electronic states

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Abstract
The equidensity orbitals (EO) are used in the resultant entropic description of molecular states which combines the probability and current contributions in the overall information content. Continuities of the modulus and phase components of electronic wavefunctions are examined, and the Harriman–Zumbach–Maschke (HZM) construction of Slater determinants yielding the prescribed electron density is explored. The conditional probability interpretation of (complex) HZM wavefunctions is formulated, the entropy/information contributions due to the state *phase* component are summarized, and a nonclassical origin of quantum dynamics of the resultant *gradient* information, related to average kinetic energy of electrons, is emphasized. The *phase* equilibria maximizing the *resultant*-entropy measures are explored, and "thermodynamic" phase minimizing the overall *gradient* information is determined. It generates finite orbital currents giving rise to the vanishing resultant flow of electrons in the system as a whole. Potential use of atomic and molecular EO bases in electronic structure calculations and interpretations in chemistry is discussed, and illustrative example of Gaussian probability distribution is examined in some detail.

Keywords Conditional probabilities · Continuity relations · Distribution-constrained wavefunctions · Entropy/information equilibria · Equidensity orbitals · Resultant entropy/information

1 Introduction

The classical information theory (IT) [1–4] explores functionals of the entropy/information content in molecular probability distribution $p(\boldsymbol{r})=\rho(\boldsymbol{r})/N$, the *shape* factor of electron density $\rho(\boldsymbol{r})$ in N-electron system. For example, the local (gradient) information measure $I[p]$ of Fisher [1, 2] and the global (logarithmic) entropy descriptor $S[p]$ of Shannon [3, 4] reflect the complementary "narrowness" and "spread" aspects of electron distributions. In accordance with modern density functional theory (DFT) [5–10], the ground-state densities $\rho_0(\boldsymbol{r})$ or $p_0(\boldsymbol{r})$ determine all molecular properties, e.g., the electronic energy for the given external potential $v(\boldsymbol{r})$ due to the system fixed nuclei, $E_0=E_v[\rho_0]=E_v[N, p_0]$, and its *classical* entropy/information contents: $S_0=S[p_0]$ or $I_0=I[p_0]$. However, in general (*non*-stationary) quantum states or for approximate (trial) wavefunctions of molecular information principles one has to take into account also the nonclassical entropy/information contributions due to the state *phase* distribution $\phi(\boldsymbol{r})$, $S[\phi]$ or $I[\phi]$ [11–15], in the *resultant*-entropy/information measures $S[p, \phi]=S[p]+S[\phi]$ or $I[p, \phi]=I[p]+I[\phi]$.

The extrema of such overall global or gradient entropy descriptors determine the *phase* equilibria in molecules and their fragments [15–20]. These generalized IT descriptors allow one to distinguish the information content of states exhibiting the same electron density but differing in their current composition, e.g., the bonded (entangled) and nonbonded (disentangled) states of subsystems in the chemical reactivity theory [21, 22]. The entropic phase contributions play an important role in an information description of

The following notation is adopted: A denotes a *scalar*, $\boldsymbol{A}$ is the row or column *vector*, $\mathbf{A}$ represents a square or rectangular *matrix*, and the dashed symbol $\hat{\mathbf{A}}$ stands for the quantum–mechanical *operator* of the physical property A. The logarithm of Shannon's information measure is taken to an arbitrary but fixed base: $\log=\log_2$ corresponds to the information content measured in *bits* (binary digits), while $\log=\ln$ expresses the amount of information in *nats* (natural units): 1 nat = 1.44 bits.

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reactive systems [23–28] by precisely specifying the mutually open (bonded) and closed (nonbonded) states of reactants. To paraphrase Prigogine [29], the density distribution establishes the molecular "static" structure *of being*, while the current pattern establishes the complementary "dynamical" aspect of molecular organization—the structure *of becoming*: the latter determines the dynamics of the former.

The classical IT of Fisher and Shannon [1–4, 30–33] has been already successfully applied to interpret molecular probability distributions, e.g., [15, 34–37]. Information principles have been explored, and density pieces attributed to atoms-in-molecules (AIM) have been approached [38–46], providing the information basis for the intuitive (stockholder) division of Hirshfeld [47]. Patterns of chemical bonds have been extracted from electronic communications in molecules [15, 34–37, 48–58], and the entropy/information distributions in molecules have been explored [15, 34–37, 59, 60]. The nonadditive Fisher information [15, 34–37, 61, 62] has been linked [62] to electron localization function (ELF) [63–65] of modern DFT. This analysis has also formulated the contragradience (CG) probe [66] for determining the bond patterns in molecules, and orbital communication theory (OCT) has identified the *bridge* interactions originating from cascade propagations of information, which involve intermediate orbitals [15, 37, 67–72].

In present analysis, the phase/current feature of electronic states will be emphasized throughout. General quantum states of N electrons yielding the prescribed electron density involve Slater determinants constructed from the (orthonormal) (*plane*-wave)-type equidensity orbitals (EO) of Harriman, Zumbach and Maschke (HZM) [73, 74], each generating the specified molecular probability distribution and exhibiting the *density*-dependent local phase safeguarding the orbital orthogonality. This construction separates the modulus and phase aspects of *multi*-electronic states thus offering an attractive framework for studying the role of classical (probability) and nonclassical (current) entropy/information contributions in chemical processes. We shall examine the construction of orbital phases and electronic currents they generate, providing them an appropriate probabilistic interpretation in terms of conditional probabilities involving electron coordinates. This development will be illustrated for the special case of the Gaussian-type probability distributions.

The continuities of the *physical*, probability and phase descriptors of electronic states implied by the Schrödinger equation will be summarized, and probability interpretation of the key constructs of this orbital representation will be given. The dynamics of resultant gradient information will be explored, and a nonclassical character of the information production will be emphasized. The overlap extension of the equidensity orbitals [75] will be outlined, and possible applications of EO bases of constituent atoms in electronic structure calculations and interpretations in chemistry will be explored.

2 Continuities of probability and phase distributions

The evolution of molecular electronic wavefunctions is determined by the Schrödinger equation (SE) of quantum mechanics. It also determines the dynamics of *probability*- and *current* attributes of the abstract (complex) quantum states [26–28] and the associated information contributions. It is of interest to examine general implications of SE for the dynamics of these two physical descriptors of the modulus and phase components of molecular wavefunctions.

For simplicity, let us first consider a single electron at time t in state $|\psi(t)\rangle \equiv |\psi\rangle$, described by the (complex) wavefunction in position representation,

$$\psi(\boldsymbol{r},t) = \langle \boldsymbol{r}|\psi(t)\rangle = R(\boldsymbol{r},t)\,\exp[\mathrm{i}\phi(\boldsymbol{r},t)], \tag{1}$$

where the real functions $R(\boldsymbol{r}, t)$ and $\phi(\boldsymbol{r}, t)$ stand for its modulus and phase parts, respectively. They determine the electron probability distribution at time t,

$$p(\boldsymbol{r},t) = \langle\psi(t)|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\psi(t)\rangle = \psi(\boldsymbol{r},t)^{*}\psi(\boldsymbol{r},t) = R(\boldsymbol{r},t)^{2}, \tag{2}$$

and the corresponding current density

$$\begin{aligned}\boldsymbol{j}(\boldsymbol{r},t) &= \left[\hbar/(2m\mathrm{i})\right]\left[\psi(\boldsymbol{r},t)^{*}\nabla\psi(\boldsymbol{r},t) - \psi(\boldsymbol{r},t)\nabla\psi(\boldsymbol{r},t)^{*}\right]\\ &= (\hbar/m)p(\boldsymbol{r},t)\nabla\phi(\boldsymbol{r},t) \equiv p(\boldsymbol{r},t)\boldsymbol{V}(\boldsymbol{r},t).\end{aligned} \tag{3}$$

Here, the effective velocity of the probability "fluid," $\boldsymbol{V}(\boldsymbol{r}, t) = \mathrm{d}\boldsymbol{r}/\mathrm{d}t$, measures the local current per particle and reflects the state *phase*-gradient:

$$\boldsymbol{V}(\boldsymbol{r},t) = \boldsymbol{j}(\boldsymbol{r},t)/p(\boldsymbol{r},t) = (\hbar/m)\nabla\phi(\boldsymbol{r},t). \tag{4}$$

The state probability density $p(\boldsymbol{r}, t)$ and its flux $\boldsymbol{j}(\boldsymbol{r}, t)$ thus constitute two independent *physical* degrees-of-freedom of such a general quantum state of an electron:

$$\psi \Leftrightarrow (R,\phi) \Leftrightarrow (p,\boldsymbol{j}). \tag{5}$$

The *phase* component of molecular states reflects the coherence, current aspect of the system electronic structure.

In molecular scenario, the electron is moving in the external potential $v(\boldsymbol{r})$ due to the "frozen" nuclei of the familiar Born–Oppenheimer (BO) approximation, thus being described by the Hamiltonian

$$\hat{\mathrm{H}}(\boldsymbol{r}) = -\left(\hbar^{2}/2m\right)\nabla^{2} + v(\boldsymbol{r}) \equiv \hat{\mathrm{T}}(\boldsymbol{r}) + v(\boldsymbol{r}), \tag{6}$$

where $\hat{\mathrm{T}}(\boldsymbol{r})$ denotes its kinetic part. The dynamics of its quantum state $\psi(\boldsymbol{r}, t)$ is determined by SE,

$$\partial\psi(\boldsymbol{r},t)/\partial t = (i\hbar)^{-1}\hat{\mathrm{H}}(\boldsymbol{r})\psi(\boldsymbol{r},t), \tag{7}$$

which also generates the associated temporal evolutions of the state probability density and of its phase distribution.

The SE implies the sourceless continuity relation for the particle probability "fluid":

$$\begin{aligned} &\partial p(\boldsymbol{r},t)/\partial t = -\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) \quad \text{or} \\ &\mathrm{d}p(\boldsymbol{r},t)/\mathrm{d}t \equiv \sigma_p(\boldsymbol{r},t) = \partial p(\boldsymbol{r},t)/\partial t + \nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0. \end{aligned} \tag{8}$$

The total *time* derivative $\mathrm{d}p(\boldsymbol{r},t)/\mathrm{d}t$ of the electron *probability* density $p(\boldsymbol{r},t)=p[\boldsymbol{r}(t),t]$ defines its local production $\sigma_p(\boldsymbol{r},t)$. It measures the time rate of change in an infinitesimal volume element around $\boldsymbol{r}(t)$ of the probability fluid moving with the local velocity $\mathrm{d}\boldsymbol{r}/\mathrm{d}t=\boldsymbol{V}(\boldsymbol{r},t)$, while the partial derivative $\partial p(\boldsymbol{r},t)/\partial t$ refers to the volume element around the fixed point in space. The vanishing total derivative $\mathrm{d}p/\mathrm{d}t$ of electron *probability* density thus reads:

$$\begin{aligned} \mathrm{d}p/\mathrm{d}t \equiv \sigma_p &= \partial p/\partial t + (\mathrm{d}\boldsymbol{r}/\mathrm{d}t)\cdot(\partial p/\partial \boldsymbol{r}) \\ &= \partial p/\partial t + \boldsymbol{V}\cdot\nabla p = 0 \quad \text{or} \\ \partial p/\partial t &= -\boldsymbol{V}\cdot\nabla p = -(\hbar/m)\nabla\phi\cdot\nabla p. \end{aligned} \tag{9}$$

Using the *probability* continuity also gives:

$$\begin{aligned} \partial p/\partial t &= -\nabla\cdot\boldsymbol{j} = -\boldsymbol{V}\cdot\nabla p - p\nabla\cdot\boldsymbol{V} \\ &= -(\hbar/m)[\nabla\phi\cdot\nabla p + p\nabla^2\phi]. \end{aligned} \tag{10}$$

Therefore, comparing the two preceding equations implies the vanishing divergence of the effective velocity field, determined by the Laplacian of the *phase* component of molecular quantum states:

$$\nabla\cdot\boldsymbol{V} = (\hbar/m)\nabla^2\phi = 0. \tag{11}$$

The probability continuity of Eq. (9) also determines the state *modulus* dynamics:

$$\partial R/\partial t = -(\hbar/m)\nabla\phi\cdot\nabla R, \tag{12}$$

while the *phase* dynamics from SE reads:

$$\partial\phi/\partial t = \left[\hbar/(2m)\right]\left[R^{-1}\Delta R - (\nabla\phi)^2\right] - v/\hbar. \tag{13}$$

The *probability* velocity $\boldsymbol{V}$ also drives the *phase* current

$$\boldsymbol{J}(\boldsymbol{r},t) \equiv \phi(\boldsymbol{r},t)\boldsymbol{V}(\boldsymbol{r},t) = (\hbar/m)\phi(\boldsymbol{r},t)\nabla\phi(\boldsymbol{r},t). \tag{14}$$

The SE then predicts a nonvanishing *phase* source in the associated continuity equation:

$$\begin{aligned} \sigma_\phi(t) \equiv \mathrm{d}\phi(t)/\mathrm{d}t &= \partial\phi(t)/\partial t + \nabla\cdot\boldsymbol{J}(t) \\ &= \partial\phi(t)/\partial t + \boldsymbol{V}(t)\cdot\nabla\phi(t) \neq 0 \quad \text{or} \\ \partial\phi(t)/\partial t - \sigma_\phi(t) &= -\nabla\cdot\boldsymbol{J}(t) = -(\hbar/m)[\nabla\phi(t)]^2. \end{aligned} \tag{15}$$

Using Eq. (13) finally gives the following production term of a local phase:

$$\sigma_\phi = \left[\hbar/(2m)\right]\left[R^{-1}\nabla^2 R + (\nabla\phi)^2\right] - v/\hbar. \tag{16}$$

It follows from these continuity relations that a common velocity of the *probability* and *phase* currents, determined by the state *phase*-gradient, reflects the structure *dynamical* aspect, while the probability density at the specified time establishes its *static* facet. The former characterizes the temporal evolution of the latter. In other words, a structure of "becoming" determines the evolution of an instantaneous structure of "being."

3 Equidensity orbitals

In DFT, one often explores the *density*-constrained ("entropic") variational principles, e.g., the Levy [7] construction of the universal density functional for the sum of electronic kinetic and repulsion energies. They are also called the "vertical" or "thermodynamic" searches, by analogy to the *minimum-energy* and *maximum-entropy* criteria for determining equilibria in ordinary thermodynamics [76]. A related problem of constructing the antisymmetric wave functions of N fermions yielding the prescribed density $\rho(\boldsymbol{r})$, vital for solving the familiar N-representability problem of DFT, has been solved by Harriman [73], who had used the crucial insights due to Macke [77, 78] and Gilbert [79]. Its *three*-dimensional generalization by Zumbach and Maschke [74] introduces the complete set of Slater determinants build using the *density*-dependent (orthonormal) equidensity orbitals (EO) of the *plane*-wave type,

$$\begin{aligned} \varphi_{\boldsymbol{q}}(\boldsymbol{r}) &= \left[\rho(\boldsymbol{r})/N\right]^{1/2}\exp\left\{i\left[\boldsymbol{q}\cdot\boldsymbol{f}(\boldsymbol{r}) + \phi(\boldsymbol{r})\right]\right\} \\ &\equiv \left[p(\boldsymbol{r})\right]^{1/2}\exp\left\{i\left[F_{\boldsymbol{q}}(\boldsymbol{r}) + \phi(\boldsymbol{r})\right]\right\} \equiv R(\boldsymbol{r})\exp\left[i\Phi_{\boldsymbol{q}}(\boldsymbol{r})\right], \end{aligned} \tag{17}$$

each generating the molecular probability distribution

$$p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N = p(x\wedge y\wedge z) \equiv p(x,y,z), \tag{18}$$

the *shape* factor of the system electron density $\rho(\boldsymbol{r})$. Here,

$$\boldsymbol{q} = \left(q_x\boldsymbol{i} + q_y\boldsymbol{j} + q_z\boldsymbol{k}\right) \equiv \left\{q_m\right\} \tag{19}$$

denotes the (constant) *reduced*-momentum (*wave*-number) vector, and $\Phi_{\boldsymbol{q}}(\boldsymbol{r})$ stands for the EO *resultant* phase, defined by the sum of the *orthogonality*-phase $F_{\boldsymbol{q}}(\boldsymbol{r})$ and *thermodynamic*-phase contribution $\phi(\boldsymbol{r})$, common to all occupied EO. The latter has to be eventually determined from the auxiliary maximum *resultant*-entropy principle, which establishes the system *phase* equilibrium. The vector function in Eq. (17),

$$\boldsymbol{f}(\boldsymbol{r}) = f_x(\boldsymbol{r})\boldsymbol{i} + f_y(\boldsymbol{r})\boldsymbol{j} + f_z(\boldsymbol{r})\boldsymbol{k} = \boldsymbol{f}[p;\boldsymbol{r}] \equiv \left\{f_m(\boldsymbol{r})\right\}, \tag{20}$$

ultimately generates the *probability*-dependent Jacobian determinant $\partial\boldsymbol{f}/\partial\boldsymbol{r} = |\partial f_m/\partial x_n|$ grouping partial derivatives $\{\partial f_m/\partial x_n\}$ of the *phase*-vector $\boldsymbol{f}\equiv\{f_m\}$ components with respect to *electron* position coordinates $\boldsymbol{r}\equiv\{x_n\}$.

This construction can be thus viewed as transformation of the physical space into itself: for any $\boldsymbol{r}=(x, y, z) \in \mathfrak{R}^3$ we define the (invertible) *density*-dependent transformation of $\boldsymbol{r}$ into the new vector $\boldsymbol{f}(\boldsymbol{r}) \in \mathfrak{R}^3$, with the familiar *plane*-wave type orthogonality relation between orbitals. The overall phase $\Phi_{\boldsymbol{q}}(\boldsymbol{r})$ of EO involves the *orbital*-specific (geometric) *internal* contribution $\boldsymbol{q}\cdot\boldsymbol{f}(\boldsymbol{r}) \equiv F_{\boldsymbol{q}}(\boldsymbol{r})$, which enforces the independence of these *one*-particle states, and "thermodynamic" *external* phase $\phi(\boldsymbol{r})$, common to all EO,

$$\Phi_{\boldsymbol{q}}(\boldsymbol{r}) = F_{\boldsymbol{q}}(\boldsymbol{r}) + \phi(\boldsymbol{r}). \tag{21}$$

The latter has to be determined from a subsidiary variational principle for the extremum of the state resultant entropy [12–21, 36].

By definition, in the HZM construction one sets this transformation between local *volume* elements as being proportional to molecular probability distribution, $\mathrm{d}\boldsymbol{f}(\boldsymbol{r}) \propto p(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$, with the associated Jacobian determinant

$$\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} = \frac{(2\pi)^3}{N}\rho(\boldsymbol{r}) = (2\pi)^3 p(\boldsymbol{r}). \tag{22}$$

As explicitly proposed by Zumbach and Maschke [74], the functional relations defining components of the phase vector field $\boldsymbol{f} = \boldsymbol{f}[\rho]$ read:

$$\begin{aligned} f_x(x,y,z) &= 2\pi \frac{\int_{-\infty}^{x} \mathrm{d}x'\, \rho(x',y,z)}{\int_{-\infty}^{\infty} \mathrm{d}x'\, \rho(x',y,z)}, \\ f_y(y,z) &= 2\pi \frac{\int_{-\infty}^{y} \mathrm{d}y' \int_{-\infty}^{\infty} \mathrm{d}x'\, \rho(x',y',z)}{\int_{-\infty}^{\infty} \mathrm{d}y' \int_{-\infty}^{\infty} \mathrm{d}x'\, \rho(x',y',z)}, \\ f_z(z) &= \frac{2\pi}{N} \int_{-\infty}^{z} \mathrm{d}z' \int_{-\infty}^{\infty} \mathrm{d}y' \int_{-\infty}^{\infty} \mathrm{d}x'\, \rho(x',y',z'). \end{aligned} \tag{23}$$

They define the functional determinant of Eq. (22):

$$\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} = \begin{vmatrix} \frac{\partial f_x}{\partial x} & 0 & 0 \\ \frac{\partial f_x}{\partial y} & \frac{\partial f_y}{\partial y} & 0 \\ \frac{\partial f_x}{\partial z} & \frac{\partial f_y}{\partial z} & \frac{\partial f_z}{\partial z} \end{vmatrix} = \left(\frac{\partial f_x}{\partial x}\right)\left(\frac{\partial f_y}{\partial y}\right)\left(\frac{\partial f_z}{\partial z}\right). \tag{24}$$

These "diagonal" derivatives $\{\partial f_\alpha/\partial x_\alpha\}$ can be expressed in terms of the relevant *conditional* probabilities [14] involving the position coordinates (see Figs. 1 and 2), defined by the corresponding ratios of the relevant *joint* probabilities:

$$\begin{aligned} \left(\frac{\partial f_x}{\partial x}\right) &= 2\pi\, p(\boldsymbol{r}) \Big/ \int_{-\infty}^{+\infty} p(\boldsymbol{r})\, \mathrm{d}x \\ &= 2\pi p(x,y,z)/p(y,z) \equiv 2\pi\, p(x|y,z), \\ \left(\frac{\partial f_y}{\partial y}\right) &= 2\pi \int_{-\infty}^{+\infty} p(x,y,z)\ \mathrm{d}x \Big/ \int_{-\infty-\infty}^{+\infty+\infty} p(x,y,z)\ \mathrm{d}x\,\mathrm{d}y \\ &= 2\pi \big[p(y,z)/p(z)\big] \equiv 2\pi\, p(y|z), \\ \left(\frac{\partial f_z}{\partial z}\right) &= 2\pi \int_{-\infty-\infty}^{+\infty+\infty} p(x,y,z)\ \mathrm{d}x\,\mathrm{d}y = 2\pi\, p(z). \end{aligned} \tag{25}$$

Here, $p(a|b) \equiv p(a, b)/p(b)$ denotes the *conditional* probability of event a, given event b, while $p(a, b)$ stands for the *joint* probability of simultaneously observing the two events. Substituting Eq. (25) into Eq. (24) then indeed generates the postulated *density*-dependent transformation between the volume elements $\mathrm{d}\boldsymbol{r}$ and $\mathrm{d}\boldsymbol{f}$:

$$\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} = (2\pi)^3 \left[\frac{p(\boldsymbol{r})}{p(y,z)}\right]\left[\frac{p(y,z)}{p(z)}\right] p(z) = (2\pi)^3 p(\boldsymbol{r}). \tag{26}$$

The mutual orthogonality between such EO states then directly follows:

$$\begin{aligned} \int_{-\infty}^{\infty} \varphi^*_{\boldsymbol{q}'}(\boldsymbol{r})\varphi_{\boldsymbol{q}}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} &= \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{f}(\boldsymbol{r})} p(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}. \\ &= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \mathrm{e}^{i(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{f}(\boldsymbol{r})} \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} \mathrm{d}\boldsymbol{r} \\ &= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \mathrm{e}^{i(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{f}} \mathrm{d}\boldsymbol{f} = \delta(\boldsymbol{q}-\boldsymbol{q}'). \end{aligned} \tag{27}$$

In "Appendix 1," the illustrative case of Gaussian probability distribution is examined, where the key concepts of HZM construction have been examined, with the local *phase* vector $\boldsymbol{f}(\boldsymbol{r})$ expressed in terms of the *error* function of probability theory.

To summarize, the Slater determinants build from specific selections of N different equidensity orbitals,

$$\begin{aligned} &\Psi_{\boldsymbol{q}_1,\boldsymbol{q}_1,\ldots,\boldsymbol{q}_N}(N) = (1/\sqrt{N!})\det(\varphi_{\boldsymbol{q}_1}, \varphi_{\boldsymbol{q}_2}, \ldots, \varphi_{\boldsymbol{q}_N}) \equiv \Psi_{\mathbf{q}}(N) \equiv \langle \mathbf{r} \mid \mathbf{q} \rangle, \\ &\{\boldsymbol{q}_i \neq \boldsymbol{q}_j\},\ \ \mathbf{r} = \{\boldsymbol{r}_i\},\ \ \mathbf{q} = \{\boldsymbol{q}_i\}, \end{aligned} \tag{28}$$

then by construction generate the prescribed electron density $\rho(\boldsymbol{r})$:

$$\left\langle \Psi_{\mathbf{q}} \middle| \hat{\rho}(\boldsymbol{r}) \middle| \Psi_{\mathbf{q}} \right\rangle = \sum_{i=1}^{N} \left|\varphi_{\boldsymbol{q}_i}(\boldsymbol{r})\right|^2 = \rho(\boldsymbol{r}). \tag{29}$$

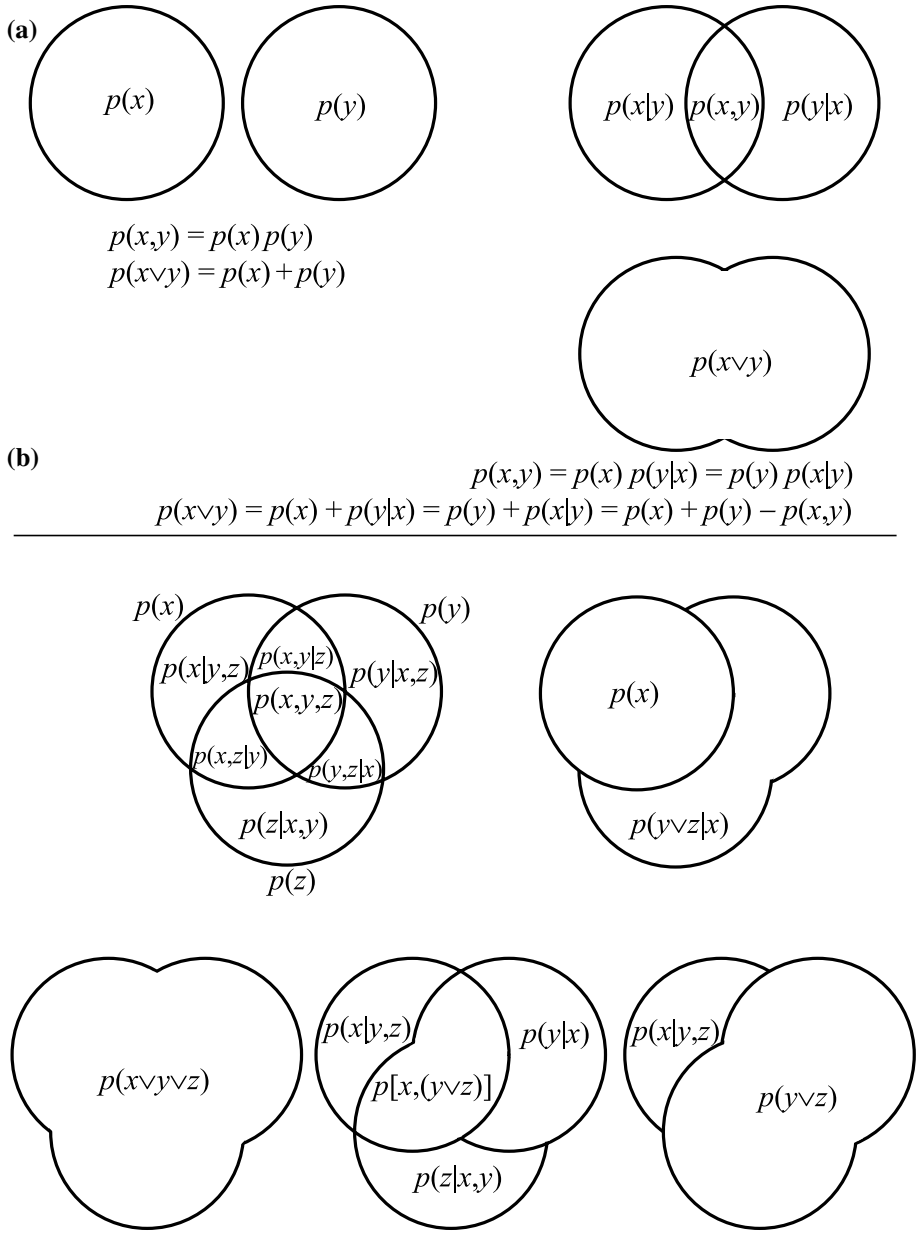

Fig. 1 The graphical representation of various *joint* and *conditional* probabilities of the electron position coordinates, $\boldsymbol{r}=x\boldsymbol{i}+y\boldsymbol{j}+z\boldsymbol{k}\equiv(x\wedge y\wedge z)\equiv(x, y, z)$, e.g., $p(\boldsymbol{r})=p(x\wedge y\wedge z)\equiv p(x, y, z)$, $p(y|x)=p(x, y)/p(x)$, $p(x,y|z)=p(x,y,z)/p(z)$, $p(x|y,z)=p[x,y,z)]/p(y,z)$, etc. A *single* circle delineates probability of a *separate* coordinate, e.g., $p(x)=\int p(\boldsymbol{r})\mathrm{d}y\mathrm{d}z$, the envelope of the two or three overlapping circles represents the probability of the *union* (sum) of observing the specified (dependent) coordinates, e.g., $p(x\vee y)=p(x)+p(y)-p(x,y)=p(x)+p(y|x)$ or $p(x\vee y\vee z)=p(x)+p(y\vee z|x)=p(y\vee z)+p(x|y,z)=[p(x|y,z)+p(y|x,z)+p(z|x,y)]+[p(y,z|x)+p(x,z|y)+p(x,y|z)]+p(x,y,z)$. The probabilities of the *joint* coordinate events (products), e.g., $p(x,y)$ or $p(x,y,z)$ similarly correspond to the overlap areas (intersections) of two or three circles, respectively. The *non*-overlapping circles in part (a) represent the independent, exclusive coordinate events

They constitute the complete orthonormal set of N-particle functions capable of representing the molecular *ground* state of N electrons for the associated electron distribution $\rho_0(\boldsymbol{r})=\rho[N, v;\boldsymbol{r}]$, the equilibrium density for the system electronic Hamiltonian

$$\hat{\mathrm{H}}(N, v)=\hat{\mathrm{V}}_{ne}(N, v)+[\hat{\mathrm{T}}(N)+\hat{\mathrm{V}}_{ee}(N)]\equiv\sum_{i=1}^{N}v(i)+\hat{\mathrm{F}}(N), \tag{30}$$

in the HZM *configuration interaction* (CI) type expansion:

$$\Psi_0(N)=\int\Psi_{\mathbf{q}}(N)C_0(\mathbf{q})\mathrm{d}\mathbf{q}. \tag{31}$$

It should be emphasized, however, that such *trial* functions do not satisfy the phase constraint of Eq. (11), the implication of the *probability*-continuity relation, since $\nabla\cdot\boldsymbol{f}(\boldsymbol{r})\neq 0$. This phase requirement should be ultimately fulfilled by the exact solutions of SE, which reflect the system dynamical conditions.

The EO $\{\varphi_{\boldsymbol{q}}(\boldsymbol{r})=\langle\boldsymbol{r}|\varphi_{\boldsymbol{q}}\rangle\equiv\langle\boldsymbol{r}|\boldsymbol{q}\rangle\}$ constitute the complete set of functions capable of representing any quantum state $|\psi\rangle$ of a single electron or the associated wavefunction in the *position* representation:

$$\psi(\boldsymbol{r})=\langle\boldsymbol{r}|\psi\rangle=\int\langle\boldsymbol{r}|\boldsymbol{q}\rangle\langle\boldsymbol{q}|\psi\rangle\mathrm{d}\boldsymbol{q}=\int\varphi_{\boldsymbol{q}}(\boldsymbol{r})\psi(\boldsymbol{q})\mathrm{d}\boldsymbol{q}. \tag{32}$$

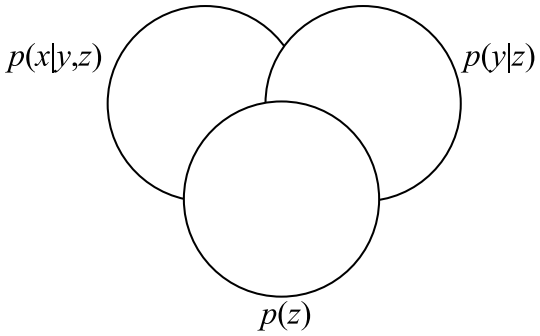

Fig. 2 Schematic diagram of the partition of the probability density $p[\mathrm{U}(\boldsymbol{r})] \equiv p(x \vee y \vee z)$ of the *union* of spatial coordinates (x, y, z) of the electron position vector $\boldsymbol{r} = x\boldsymbol{i} + y\boldsymbol{j} + z\boldsymbol{k}$ (see also Fig. 1), corresponding to the envelope of three probability circles $\{p(x_n)\}$ for the *separate* Cartesian coordinates, into partial areas representing the *conditional* probabilities of Eq. (25). Here, $p(z)$ stands for the probability distribution of the coordinate "z," $p(y|z)$ is the conditional probability of observing coordinate "y" given "z," and $p(x|y,z)$ denotes conditional probability of observing coordinate "x," when one has already simultaneously observed coordinates "y" and "z"

They constitute the basis of the *Harriman* representation of electronic states [14, 36]. The coefficient function in the preceding equation,

$$\psi(\boldsymbol{q}) = \langle \boldsymbol{q}|\psi\rangle = \int \langle \boldsymbol{q}|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi\rangle \mathrm{d}\boldsymbol{r} = \int \varphi_{\boldsymbol{q}}(\boldsymbol{r})^{*}\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \quad (33)$$

the *momentum* representation of $|\psi\rangle$ can be subsequently $(\boldsymbol{r} \rightarrow \boldsymbol{f})$-transformed,

$$\psi(\boldsymbol{q}) = \int \langle \boldsymbol{q}|\boldsymbol{f}\rangle\langle \boldsymbol{f}|\psi\rangle \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} \mathrm{d}\boldsymbol{r} \equiv \int \varphi_{\mathbf{q}}(\boldsymbol{f})^{*}\psi(\boldsymbol{f})\mathrm{d}\boldsymbol{f}, \quad (34)$$

where the transformed "volume" element

$$\mathrm{d}\boldsymbol{f} = \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{r}} \mathrm{d}\boldsymbol{r} = (2\pi)^{3} p(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}. \quad (35)$$

Here, $\psi(\boldsymbol{f}) = \langle \boldsymbol{f}|\psi\rangle$ stands for the $\boldsymbol{f}$ representation of the state vector $|\psi\rangle$, while $\varphi_{\boldsymbol{q}}(\boldsymbol{f})$ similarly expresses the state $|\varphi_{\boldsymbol{q}}\rangle$ in terms of the *density*-dependent spatial variable $\boldsymbol{f}$.

These equations summarize the Fourier transformations between the momentum ($|\boldsymbol{q}\rangle$) and position ($|\boldsymbol{r}\rangle$ or $|\boldsymbol{f}\rangle$) representations of $|\psi\rangle$. Notice that in this vector interpretation, the orthogonality relation of Eq. (27) reads,

$$\int_{-\infty}^{\infty} \phi^{*}_{\boldsymbol{q}'}(\boldsymbol{r})\phi_{\boldsymbol{q}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \int \langle \boldsymbol{q}'|\boldsymbol{r}\rangle\,\mathrm{d}\boldsymbol{r}\,\langle \boldsymbol{r}|\boldsymbol{q}\rangle = \langle \boldsymbol{q}'|\boldsymbol{q}\rangle = \delta(\boldsymbol{q} - \boldsymbol{q}'), \quad (36)$$

thus manifesting the completeness of the EO basis yielding the molecular probability density:

$$\int |\boldsymbol{r}\rangle\,\mathrm{d}\boldsymbol{r}\,\langle \boldsymbol{r}| = \int |\boldsymbol{f}\rangle\,\mathrm{d}\boldsymbol{f}\,\langle \boldsymbol{f}| = \int |\boldsymbol{q}\rangle\,\mathrm{d}\boldsymbol{q}\,\langle \boldsymbol{q}| = 1. \quad (37)$$

It is also of interest to express the HZM representation of $|\psi\rangle$, $\psi(\boldsymbol{f}) = \langle \boldsymbol{f}|\psi\rangle$, in terms of its standard position or momentum representations: $\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle$ or $\psi(\boldsymbol{k}) = \langle \boldsymbol{k}|\psi\rangle$. Using the familiar Fourier transformation gives:

$$\begin{aligned}\psi(\boldsymbol{f}) &= \int \mathrm{d}\boldsymbol{r}\langle \boldsymbol{f}|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi\rangle = \int \mathrm{d}\boldsymbol{r}\boldsymbol{f}(\boldsymbol{r})^{*}\psi(\boldsymbol{r}) \\ &= \int \mathrm{d}\boldsymbol{k}\langle \boldsymbol{f}|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\psi\rangle = \int \mathrm{d}\boldsymbol{k}\boldsymbol{f}(\boldsymbol{k})^{*}\psi(\boldsymbol{k}) \\ &= \int \mathrm{d}\boldsymbol{k}[(2\pi)^{-3/2} \int \mathrm{d}\boldsymbol{r}\exp(-i\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{f}(\boldsymbol{r})]\psi(\boldsymbol{k}),\end{aligned} \quad (38)$$

with $\boldsymbol{f}(\boldsymbol{k}) = \langle \boldsymbol{k}|\boldsymbol{f}\rangle$ and $\boldsymbol{f}(\boldsymbol{r}) = \langle \boldsymbol{r}|\boldsymbol{f}\rangle = \boldsymbol{r}(\boldsymbol{f})^{*}$ standing for the momentum and position representations of $|\boldsymbol{f}\rangle$, respectively.

The admissible N-electron determinants $\Psi_{\mathbf{q}}(\mathbf{r}) \equiv \left\langle \{\boldsymbol{r}_i\} \,\middle|\, \Psi_{\mathbf{q}} \right\rangle \equiv \langle \mathbf{r} \mid \mathbf{q}\rangle$ similarly span the complete N-electron basis in molecular Hilbert space,

$$\begin{aligned}&\int |\mathbf{r}\rangle\,\mathrm{d}\mathbf{r}\,\langle \mathbf{r}| = \int |\mathbf{f}\rangle\,\mathrm{d}\mathbf{f}\,\langle \mathbf{f}| = \int |\mathbf{q}\rangle\,\mathrm{d}\mathbf{q}\,\langle \mathbf{q}| = 1, \quad \mathbf{f} = \{f(\boldsymbol{r}_i) \equiv f_i\}, \\ &\mathrm{d}\mathbf{r} = \prod_i \mathrm{d}\boldsymbol{r}_i, \quad \mathrm{d}\mathbf{q} = \prod_i \mathrm{d}\boldsymbol{q}_i, \quad \mathrm{d}\mathbf{f} = \prod_i \mathrm{d}f_i,\end{aligned} \quad (39)$$

which can be used in the CI-type expansion of Eq. (31) for the molecular ground state $|\Psi_0\rangle$:

$$\begin{aligned}\Psi_0(\mathbf{r}) &= \langle \mathbf{r}|\Psi_0\rangle = \int \langle \mathbf{r}|\mathbf{q}\rangle\langle \mathbf{q}|\Psi_0\rangle \mathrm{d}\mathbf{q} \\ &\equiv \int \mathbf{r}(\mathbf{q})^{*}\Psi_0(\mathbf{q})\mathrm{d}\mathbf{q} = \Psi_0(N).\end{aligned} \quad (40)$$

4 Resultant descriptors, *phase* equilibria and information production

For simplicity, let us first consider a single electron in the specified quantum state $|\psi\rangle$ of Eq. (1). The average Fisher's [1, 2] measure of the gradient information for *locality* events contained in the electronic probability density $p(\boldsymbol{r}) = R(\boldsymbol{r})^2$ [80], called the intrinsic accuracy, is reminiscent of von Weizsäcker's [81] inhomogeneity correction to *kinetic* energy functional,

$$\begin{aligned}I[p] &= \langle \psi|(\nabla \ln p)^2|\psi\rangle = \int [\nabla p(\boldsymbol{r})]^2/p(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &= 4\int [\nabla R(\boldsymbol{r})]^2 \mathrm{d}\boldsymbol{r} \equiv I[R].\end{aligned} \quad (41)$$

This classical measure characterizes an effective "narrowness" of the spatial probability distribution, a degree of electronic *position* determinicity. It represents the complementary measure to Shannon's [3, 4] global entropy descriptor,

$$S[p] = -\langle\psi|\ln p|\psi\rangle = -\int p(\boldsymbol{r})\ln p(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = -2\int R(\boldsymbol{r})^2\ln R(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \equiv S[R], \tag{42}$$

which reflects the *position* uncertainty, i.e., a "spread" of the distribution.

In quantum IT (QIT), these complementary classical descriptors are supplemented by the associated nonclassical complements in the *resultant*-entropy/information functionals, which combine the probability and phase/current contributions. The intrinsic accuracy concept generalizes naturally into the associated *resultant* descriptor of the gradient information content in the quantum state $|\psi\rangle$ itself:

$$I[\psi] = I[p] + I[\phi] \equiv I[p,\phi] = I[p] + I[\boldsymbol{j}] \equiv I[p,\boldsymbol{j}]. \tag{43}$$

This overall *Fisher*-type measure is defined by the expectation value of the Hermitian information operator $\hat{\mathrm{I}}(\boldsymbol{r})$ [61], related to kinetic energy operator $\hat{\mathrm{T}}(\boldsymbol{r})$ of Eq. (6),

$$\hat{\mathrm{I}}(\boldsymbol{r}) = -4\Delta = (8m/\hbar^2)\,\hat{\mathrm{T}}(\boldsymbol{r}) \equiv \sigma\hat{\mathrm{T}}(\boldsymbol{r}). \tag{44}$$

Using the integration by parts then gives:

$$\begin{aligned} I[\psi] &= \langle\psi|\hat{\mathrm{I}}|\psi\rangle = -4\int \psi(\boldsymbol{r})^*\Delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = 4\int |\nabla\psi(\boldsymbol{r})|^2\mathrm{d}\boldsymbol{r} \\ &= I[p] + 4\int p(\boldsymbol{r})[\nabla\phi(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \equiv I[p] + I[\phi] = I[p,\phi] \\ &= I[p] + (2m/\hbar)^2\int p(\boldsymbol{r})^{-1}\boldsymbol{j}(\boldsymbol{r})^2\mathrm{d}\boldsymbol{r} \equiv I[p] + I[\boldsymbol{j}] = I[p,\boldsymbol{j}] \end{aligned} \tag{45}$$

This quantum information concept thus combines the classical (probability) contribution $I[p]$ of Fisher and (positive) nonclassical (phase/current) supplement $I[\phi] = I[\boldsymbol{j}]$. The sign of the latter expresses the fact that nonvanishing *current* pattern introduces more structural *determinicity* or *order* information about the system. This dimensionless measure is seen to also reflect the average kinetic energy of an electron

$$T[\psi] = \langle\psi|\hat{\mathrm{T}}|\psi\rangle = \sigma^{-1}I[\psi]. \tag{46}$$

It is of interest to examine the resultant *gradient* information content of EO. One first observes that $\varphi_{\boldsymbol{q}}(\boldsymbol{r})$. satisfies the *pseudo*-eigenvalue problem of the momentum operator $\hat{\mathbf{p}}(\boldsymbol{r}) = -i\hbar\nabla$,

$$\hat{\mathbf{p}}(\boldsymbol{r})\;\varphi_{\boldsymbol{q}}(\boldsymbol{r}) = -i\hbar\nabla\varphi_{\boldsymbol{q}}(r) = -i\hbar 1/2\nabla\ln p(\boldsymbol{r}) + i\boldsymbol{q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r})]\varphi_{\boldsymbol{q}}(\boldsymbol{r}), \tag{47}$$

which directly gives the expectation value of the information operator of Eq. (44):

$$\begin{aligned} I[\varphi_{\boldsymbol{q}}] &= (4/\hbar^2)\boldsymbol{p}^2[\varphi_{\boldsymbol{q}}] = (4/\hbar^2)\langle\varphi_{\boldsymbol{q}}|\hat{\mathbf{p}}^2|\varphi_{\boldsymbol{q}}\rangle = 4\int |\nabla\varphi_{\boldsymbol{q}}(\boldsymbol{r})|^2\mathrm{d}\boldsymbol{r} \\ &= \int p(\boldsymbol{r})^{-1}[\nabla p(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} + 4\boldsymbol{q}^2\int p(\boldsymbol{r})[\nabla\cdot\boldsymbol{f}(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \equiv I[p] + I[F_{\boldsymbol{q}}]. \end{aligned} \tag{48}$$

Its first (classical) contribution thus amounts to the Fisher information in probability distribution $p(\boldsymbol{r})$, while the second (nonclassical) component, due to the *orthogonality* phase of Eq. (17), amounts to the *plane*-wave contribution $4\boldsymbol{q}^2$ multiplied by the EO-average value of the squared divergence of the phase vector field $\boldsymbol{f}(\boldsymbol{r})$.

One similarly generalizes the global entropy concept by supplementing the classical (probability) functional with the (negative) nonclassical contribution generated by the state (positive) phase [15–21]. Its sign implies a decrease in state overall structural *indeterminicity* due to its nonvanishing current distribution. The resultant *global* entropy measure then reads

$$\begin{aligned} S[\psi] &= -\langle\psi|\ln p + 2\phi|\psi\rangle = S[p] - 2\int p(\boldsymbol{r})\phi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &\equiv S[p] + S[\phi] \equiv S[p,\phi], \end{aligned} \tag{49}$$

while the overall *gradient* entropy is given by the expectation value

$$\begin{aligned} M[\psi] &= \langle\psi|(\nabla\ln p)^2 - (2\nabla\phi)^2|\psi\rangle = I[p] - I[\phi] \\ &\equiv M[p] + M[\phi] \equiv M[p,\phi]. \end{aligned} \tag{50}$$

The negative character of the phase contribution $M[\phi]$ in the latter reflects the fact that a presence of a finite current decreases the overall structure-uncertainty (entropy) content in ψ.

The state extrema of these uncertainty descriptors identify the same optimum (*non*negative) *equilibrium*-phase solution,

$$\begin{aligned} &\{\delta S[\psi]/\delta\psi^*(\boldsymbol{r}) = [-\ln p(\boldsymbol{r}) - 2\phi_{eq.}(\boldsymbol{r})]\psi(\boldsymbol{r}) = 0 \text{ or} \\ &\delta M[\psi]/\delta\psi^*(\boldsymbol{r}) = \{[\nabla\ln p(\boldsymbol{r})]^2 - [2\nabla\phi_{eq.}(\boldsymbol{r})]^2\}\,\psi(\boldsymbol{r}) = 0, \quad \phi_{eq.} \geq 0, \end{aligned} \tag{51}$$

$$\Rightarrow \phi_{eq.}(\boldsymbol{r}) = -(1/2)\ln p(\boldsymbol{r}). \tag{52}$$

This *entropy* equilibrium ("thermodynamic") phase thus generates the associated EO *current* density reflecting the negative *probability*-gradient:

$$\boldsymbol{j}_{eq.}(\boldsymbol{r}) = (\hbar/m)p(\boldsymbol{r})\nabla\phi_{eq.}(\boldsymbol{r}) = -[\hbar/(2m)]\nabla p(\boldsymbol{r}). \tag{53}$$

One also introduces the *complex* overall entropy concept [11], the quantum expectation value of the *non*-Hermitian entropy operator $\hat{\mathbf{S}}(\boldsymbol{r}) = -2\ln\psi(\boldsymbol{r})$. In this "vector" measure of the state overall structural uncertainty, the two contributions of Eq. (49) constitute its real and imaginary parts:

$$\vec{S}[\psi] \equiv \left\langle\psi\middle|\hat{\mathbf{S}}\middle|\psi\right\rangle = \langle\psi|-2\ln\psi|\psi\rangle = S[p] + iS[\phi]. \tag{54}$$

In the Schrödinger dynamical picture, the *time* evolution of resultant *gradient* information, the operator of which does not depend on time explicitly, $\hat{\mathrm{I}}(\boldsymbol{r}) = -4\nabla^2 = \sigma\hat{\mathrm{T}}(\boldsymbol{r})$, results solely from the quantum dynamics of the system *state* vector $|\psi(t)\rangle$,

determined by SE. The *time* derivative of the resultant gradient information [20],

$$\mathrm{d}I(t)/\mathrm{d}t = (i/\hbar)\left\langle \psi(t)\left|\left[\hat{\mathrm{H}},\hat{\mathrm{I}}\right]\right|\psi(t)\right\rangle, \tag{55}$$

is then generated by the expectation value of the commutator

$$\begin{aligned}\left[\hat{\mathrm{H}},\hat{\mathrm{I}}\right] &= \left[v,\hat{\mathrm{I}}\right] = 4\left[\nabla^2, v\right] = 4\{[\nabla, v]\cdot\nabla + \nabla\cdot[\nabla, v]\},\\ [\nabla, v] &= \nabla v,\end{aligned} \tag{56}$$

and the integration by parts implies:

$$\langle\psi(t)|\nabla\psi(t)\rangle = -\langle\nabla\psi(t)|\psi(t)\rangle \equiv \left\langle \nabla^{\dagger}\psi(t)|\psi(t)\right\rangle \quad \text{or} \quad \nabla^{\dagger} = -\nabla. \tag{57}$$

Hence, the integral production (source) of this information descriptor reads:

$$\begin{aligned}\sigma_I(t) \equiv \mathrm{d}I(t)/\mathrm{d}t &= (4i/\hbar)\{\langle\psi(t)|\nabla v\cdot|\nabla\psi(t)\rangle - \langle\nabla\psi(t)|\cdot\nabla v|\psi(t)\rangle\}\\ &= -(8/\hbar)\mathrm{Im}\langle\psi(t)|\nabla v\cdot|\nabla\psi(t)\rangle\\ &= -(8/\hbar)\mathrm{Im}\left[\int \psi(t) * \nabla v\cdot\nabla\psi(t)\mathrm{d}\boldsymbol{r}\right]\\ &= -(8/\hbar)\int p(t)\nabla\phi(t)\cdot\nabla v\mathrm{d}\boldsymbol{r} = -\sigma\int \boldsymbol{j}(t)\cdot\nabla v\mathrm{d}\boldsymbol{r}.\end{aligned} \tag{58}$$

This derivative is seen to be determined by the current content of molecular electronic state. Therefore, it identically vanishes for the zero-current density everywhere, when the local component of the state phase identically vanishes, thus confirming its nonclassical origin.

This qualitative conclusion also follows from the *time*-differentiation of the resultant gradient information $I[p, \phi] = I[p] + I[\phi]$ [Eq. (45)]. Its vanishing classical source then indeed directly follows from the sourceless character of probability distribution [Eq. (8)],

$$\mathrm{d}I[p]/\mathrm{d}t = \int \{\delta I[p]/\delta p(\boldsymbol{r})\}\sigma_p(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r} = 0, \tag{59}$$

while the *phase* continuity relations [Eqs. (11) and (16)] give the following expression for the nonclassical information source:

$$\begin{aligned}\mathrm{d}I[\phi]/\mathrm{d}t &= \int \{\delta I[\phi]/\delta p(\boldsymbol{r})\}\sigma_p(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r}\\ &\quad + \int \{\delta I[\phi]/\delta\phi(\boldsymbol{r})\}\sigma_\phi(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r}\\ &= \int \{\delta I[\phi]/\delta\phi(\boldsymbol{r})\}\sigma_\phi(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r}\\ &= -8\int \sigma_\phi(\boldsymbol{r}, t)\nabla p(\boldsymbol{r}, t)\cdot\nabla\phi(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r}.\end{aligned} \tag{60}$$

Therefore, the integral source of resultant *gradient* information in fact reflects the total *time* derivative of its nonclassical contribution $I[\phi]$. Hence, the associated derivative of the overall *gradient* entropy of Eq. (50) reads:

$$\sigma_M(t) \equiv \mathrm{d}M(t)/\mathrm{d}t = \mathrm{d}I\left[p\right]/\mathrm{d}t - \mathrm{d}I[\phi]/\mathrm{d}t = -\mathrm{d}I\left[\phi\right]/\mathrm{d}t = -\sigma_I(t). \tag{61}$$

This result confirms the intuitive expectation that an increase in the state overall structural *determinicity* (order) information, $\sigma_I(t) > 0$ implies the associated decrease in the structural *indeterminicity* (disorder) information (entropy): $\sigma_M(t) < 0$.

The above *one*-electron development can be straightforwardly generalized into a general *N*-electron system in the specified electronic state $|\Psi(N)\rangle$, exhibiting the electron density $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$. The *N*-electron information operator then combines terms due to each particle,

$$\hat{\mathrm{I}}(N) = \sum_{i=1}^{N}\hat{\mathrm{I}}(\boldsymbol{r}_i) = \sigma\hat{\mathrm{T}}(N), \tag{62}$$

and determines the state overall *gradient* information,

$$I(N) = \langle\Psi(N)|\hat{\mathrm{I}}(N)|\Psi(N)\rangle = \sigma\langle\Psi(N)|\hat{\mathrm{T}}(N)|\Psi(N)\rangle = \sigma T(N), \tag{63}$$

proportional to the system average kinetic energy $T(N)$. The relevant separation of the *modulus* and *phase* components of *N*-electron states calls for wavefunctions yielding the specified electron density. For example, in DFT this goal can be effected using the HZM construction, which we have outlined in Sect. 3.

5 Probability currents and *information* equilibria

Both parts of the resultant EO *phases* $\Phi_{\boldsymbol{q}}$ in Eq. (17) contribute to the overall probability current generated by the Slater determinant $\Psi_{\mathbf{q}}(N)$ describing an electron configuration. The given EO $\varphi_{\boldsymbol{q}}(\boldsymbol{r})$ generates the associated current density

$$\boldsymbol{j}_{\boldsymbol{q}}(\boldsymbol{r}) = \left\langle \varphi_{\boldsymbol{q}}\left|\hat{\mathbf{j}}(\boldsymbol{r})\right|\varphi_{\boldsymbol{q}}\right\rangle = \frac{\hbar}{m}p(\boldsymbol{r})\nabla\Phi_{\boldsymbol{q}}(\boldsymbol{r}) = \frac{\hbar}{m}p(\boldsymbol{r})\left[\boldsymbol{q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + \nabla\phi(\boldsymbol{r})\right]. \tag{64}$$

Hence, the overall current in a trial configuration of *N* electrons, corresponding to the *N*-electron operator

$$\hat{\mathbf{j}}(\boldsymbol{r}; N) = \sum_{l=1}^{N}\hat{\mathbf{j}}_l(\boldsymbol{r}), \tag{65}$$

$$\begin{aligned}\boldsymbol{j}_{\mathbf{q}}(\boldsymbol{r}) &= \langle\Psi_{\mathbf{q}}(N)|\hat{\mathbf{j}}(\boldsymbol{r}; N)|\Psi_{\mathbf{q}}(N)\rangle = \sum_{l=1}^{N}\boldsymbol{j}_{\boldsymbol{q}_l}(\boldsymbol{r})\\ &= \frac{\hbar}{m}p(\boldsymbol{r})\boldsymbol{Q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + \frac{\hbar}{m}\rho(\boldsymbol{r})\nabla\phi(\boldsymbol{r})\\ &= (\hbar/m)\rho(\boldsymbol{r})[\langle\boldsymbol{q}\rangle\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + \nabla\phi(\boldsymbol{r})] \equiv \boldsymbol{j}_f(\boldsymbol{r}) + \boldsymbol{j}_\phi(\boldsymbol{r}),\end{aligned} \tag{66}$$

where

$$\boldsymbol{Q} = \sum_{l=1}^{N} \boldsymbol{q}_l \equiv N\langle \boldsymbol{q} \rangle \tag{67}$$

denotes the resultant "*wave*-number" vector of $\Psi_{\mathbf{q}}(N)$, independent of the spatial position $\boldsymbol{r}$, and $\nabla\cdot\boldsymbol{f}(\boldsymbol{r})$ stands for the divergence of its phase vector field $\boldsymbol{f}(\boldsymbol{r})$.

A reference to Eq. (25) and Fig. 2 shows that this divergence corresponds to the probability density of the *union* (sum) $\mathrm{U}(\boldsymbol{r}) = x \vee y \vee z$ of observing the specified position coordinates,

$$\begin{aligned} \nabla\cdot\boldsymbol{f}(\boldsymbol{r}) &= \partial f_x/\partial x + \partial f_y/\partial y + \partial f_z/\partial z \\ &= 2\pi[p(x|y,z) + p(y|z) + p(z)] \\ &= 2\pi p(x \vee y \vee z) \equiv 2\pi p[U(\boldsymbol{r})] \geq 0, \end{aligned} \tag{68}$$

which is represented by the area enclosed by the envelope of three probability circles in the figure [14, 36].

Therefore, in the HZM construction of an antisymmetric wavefunction of N electrons the Jacobian of the $\boldsymbol{r} \rightarrow \boldsymbol{f}(\boldsymbol{r})$ transformation, expressing a dependence of the volume element $\mathrm{d}\boldsymbol{f}$ on the spatial volume $\mathrm{d}\boldsymbol{r}$, is proportional to molecular probability function of the *product* (joint) event involving the spatial coordinates of an electron, while its divergence—determining the current density—corresponds to the probability of the *union* of such elementary *coordinate* events.

The overall current of Eq. (66) consists of the resultant "orthogonality" component $\boldsymbol{j}_f(\boldsymbol{r})$ in HZM construction, determined by the local electron density $\rho(\boldsymbol{r})$, the average *wave*-number vector $\langle \boldsymbol{q} \rangle$ and the divergence of the *phase* vector $\boldsymbol{f}(\boldsymbol{r})$, supplemented by the overall "thermodynamic" component $\boldsymbol{j}_\phi(\boldsymbol{r})$ determined by the "thermodynamic" *phase*-gradient, $\nabla\phi(\boldsymbol{r})$. The orbital contributions $\{\boldsymbol{j}_l(\boldsymbol{r})\}$ to the former,

$$\begin{aligned} \boldsymbol{j}_f(\boldsymbol{r}) &\equiv \sum_l \boldsymbol{j}_l(\boldsymbol{r}) = [\nabla\cdot\boldsymbol{f}(\boldsymbol{r})] \cdot \sum_l \left[(\hbar/m)\boldsymbol{q}_l p(\boldsymbol{r})\right] \\ &\equiv [\nabla\cdot\boldsymbol{f}(\boldsymbol{r})] \sum_l \boldsymbol{j}(\boldsymbol{q}_l;\boldsymbol{r}) = \sum_l \{2\pi p[U(\boldsymbol{r})]\boldsymbol{j}(\boldsymbol{q}_l;\boldsymbol{r})\}, \end{aligned} \tag{69}$$

can be also regarded as the $\nabla\cdot\boldsymbol{f}(\boldsymbol{r})$-enhanced *plane*-wave currents $\boldsymbol{j}(\boldsymbol{q}_l;\boldsymbol{r})$ of $\Psi_{\mathbf{q}}(N)$, with the local enhancement factor reflecting the probability density of Fig. 2.

It is also of interest to determine the *information*-optimum thermodynamic phase, which minimizes the nonclassical gradient information of EO, for the prescribed molecular probability distribution. Indeed, in such a *vertical* search, for the fixed (ground-state) probability density $p_0 = \rho_0/N$, it is the *thermodynamic* phase $\phi(\boldsymbol{r})$ of EO states $\{\psi_l[p_0]\}$, which is being optimized, since their orthogonality phases are uniquely determined by the electron density ρ_0: $\boldsymbol{f}(\boldsymbol{r}) = \boldsymbol{f}[\rho_0;\boldsymbol{r}]$ and $\{\boldsymbol{q}_l = \boldsymbol{q}_l[\rho_0]\}$. The condition of the minimum overall gradient information in configuration $\Psi_{\mathbf{q}}[p_0]$,

$$\begin{aligned} I\left[\Psi_{\mathbf{q}}[p_0]\right] &= \sum\nolimits_l \langle \psi_l[p_0] | \left(\nabla \ln p_0\right)^2 + (2\nabla\Phi_l[\phi;p_0])^2 | \psi_l[p_0]\rangle \\ &\equiv I[p_0] + I[\phi;p_0], \end{aligned} \tag{70}$$

for the specified probability distribution p_0, the *shape* factor of ρ_0, then implies the minimum value of the overall nonclassical information,

$$\begin{aligned} I\left[\{\Phi_l[\phi;p_0]\}\right] &= 4\int p_0(\boldsymbol{r})\left\{\sum\nolimits_l \left[\nabla\Phi_l(\boldsymbol{r})\right]^2\right\}\mathrm{d}\boldsymbol{r} \\ &\equiv 4\int p_0(\boldsymbol{r})\left\{\sum\nolimits_l \left[\boldsymbol{g}_l(\boldsymbol{r})\right]^2\right\}\mathrm{d}\boldsymbol{r} \geq 0, \\ \boldsymbol{g}_l(\boldsymbol{r}) &= \nabla\Phi_l(\boldsymbol{r}) = \boldsymbol{q}_l\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + \nabla\phi(\boldsymbol{r}) \equiv \boldsymbol{g}_F(\boldsymbol{r}) + \boldsymbol{g}_\phi(\boldsymbol{r}), \end{aligned} \tag{71}$$

with respect to thermodynamic part ϕ of the resultant EO phases $\{\Phi_l[\phi;p_0]\}$:

$$\mathrm{Min}_\phi I\left[\{\Phi_l[\phi;p_0]\}\right] \equiv I\left[\{\Phi_l[\phi_{\mathrm{opt.}};p_0]\}\right] = 0. \tag{72}$$

This condition is satisfied by the optimum phase $\phi_{\mathrm{opt.}}(\boldsymbol{r})$ satisfying the local gradient condition

$$\sum\nolimits_l \left(\nabla\Phi_l[\phi_{\mathrm{opt.}};p_0]\right)^2 \equiv \sum\nolimits_l \boldsymbol{g}_l^2 \equiv G(\{\boldsymbol{g}_l\}) = 0. \tag{73}$$

This minimum value of $G(\{\boldsymbol{g}_l\})$ implies the associated Euler equation for determining the *information*-optimum thermodynamic phase $\phi_{\mathrm{opt.}}(\boldsymbol{r}) \geq 0$:

$$\begin{aligned} &\left[\partial G(\{\boldsymbol{g}_l\})/\partial\boldsymbol{g}_\phi\right] = \sum\nolimits_l \left(\partial\boldsymbol{g}_l/\partial\boldsymbol{g}_\phi\right)\left(\partial G/\partial\boldsymbol{g}_l\right)|_{\mathrm{opt.}} \\ &= 2\sum\nolimits_l \boldsymbol{g}_l[p_0,\phi_{\mathrm{opt.}}] = 0 \quad \text{or} \\ &\nabla\left(\sum_{l=1}^{N}\{\boldsymbol{q}_l\cdot\boldsymbol{f}[p_0;\boldsymbol{r}] + N\phi_{\mathrm{opt.}}[p_0;\boldsymbol{r}]\}\right) = 0. \end{aligned} \tag{74}$$

This equation thus predicts, to a constant phase unspecified in QM,

$$\begin{aligned} \phi_{\mathrm{opt.}}[p_0;\boldsymbol{r}] &= -N^{-1}\left(\sum_{l=1}^{N}\boldsymbol{q}_l[p_0]\right)\cdot\boldsymbol{f}[p_0;\boldsymbol{r}] + \text{const.} \\ &\equiv -N^{-1}\left(\boldsymbol{Q}[p_0]\right)\cdot\boldsymbol{f}[p_0;\boldsymbol{r}] + \text{const.} \\ &\equiv \langle \boldsymbol{q}[p_0]\rangle\cdot\boldsymbol{f}[p_0;\boldsymbol{r}] + \text{const.} \end{aligned} \tag{75}$$

Setting const. = 0 finally determines the optimum phase $\phi_{\mathrm{opt.}}[p_0;\boldsymbol{r}]$ of EO that minimizes their overall nonclassical gradient information $I[\phi;p_0]$ (see also "Appendix 2"):

$$\phi_{\mathrm{opt.}}[p_0;\boldsymbol{r}] = -\langle \boldsymbol{q}[p_0]\rangle\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]. \tag{76}$$

One observes that this *information*-optimum local phase of EO differs from its *entropy*-optimum ("equilibrium") analog of Eq. (52). It generates the orbital current in direction of the EO-average wave-number vector $\langle \boldsymbol{q}[p_0]\rangle$:

$$\boldsymbol{j}[\phi_{\text{opt.}}] \equiv \boldsymbol{j}_{\text{opt.}}[p_0;\boldsymbol{r}] = (\hbar/m)p_0(\boldsymbol{r})\nabla\phi_{\text{opt.}}[p_0;\boldsymbol{r}] = -(\hbar/m)\langle \boldsymbol{q}[p_0]\rangle\nabla\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]. \tag{77}$$

To summarize, the *information*-optimum thermodynamic phase of EO is determined by the average "wave-number" vector $\langle \boldsymbol{q}\rangle$ in $\Psi_{\mathbf{q}}(N)=\Psi_{\boldsymbol{q}_1,\boldsymbol{q}_1,\ldots,\boldsymbol{q}_N}(N)$. The associated *information*-"equilibrium" EO thus exhibits the *overall* phase determined by the deviation of its wave-number vector $\boldsymbol{q}_l$ from *configuration*-average vector $\langle \boldsymbol{q}\rangle$:

$$\varphi^{\text{opt.}}_{\boldsymbol{q}_l}[p_0;\boldsymbol{r}] = [p_0(\boldsymbol{r})]^{1/2}\exp(\mathrm{i}\{(\boldsymbol{q}_l[p_0]-\langle \boldsymbol{q}[p_0]\rangle)\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]\}) \equiv [p_0(\boldsymbol{r})]^{1/2}\exp\{\mathrm{i}\delta\boldsymbol{q}_l[p_0]\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]\}, \tag{78}$$

and generates the associated orbital current:

$$\boldsymbol{j}^{\text{opt.}}_{\boldsymbol{q}_l}[p_0;\boldsymbol{r}] = \frac{\hbar}{m}p_0(\boldsymbol{r})\delta\boldsymbol{q}_l[p_0]\nabla\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]. \tag{79}$$

Such *phase*-transformed EO thus gives rise to the vanishing resultant probability current:

$$\boldsymbol{j}^{\text{opt.}}_{\boldsymbol{q}}[p_0;\boldsymbol{r}] = \sum_{l=1}^{N}\boldsymbol{j}^{\text{opt.}}_{\boldsymbol{q}_l}[p_0;\boldsymbol{r}] = \frac{\hbar}{m}[Np_0(\boldsymbol{r})]\left\{\left(\frac{1}{N}\sum_{l=1}^{N}\delta\boldsymbol{q}_l[p_0]\right)\nabla\cdot\boldsymbol{f}[p_0;\boldsymbol{r}]\right\} \equiv \frac{\hbar}{m}\rho_0(\boldsymbol{r})\langle\delta\boldsymbol{q}_l[p_0]\rangle\nabla\cdot\boldsymbol{f}[p_0;\boldsymbol{r}] = 0, \tag{80}$$

since

$$\langle\delta\boldsymbol{q}\rangle = N^{-1}\left\langle\sum_l \boldsymbol{q}_l\right\rangle - \langle\boldsymbol{q}\rangle = \langle\boldsymbol{q}\rangle - \langle\boldsymbol{q}\rangle = 0. \tag{81}$$

The *information*-optimum equilibria in EO, for the specified electron density, thus ascribe finite orbital currents, which sum up to the vanishing resultant probability current in the system as a whole. Moreover, since in the *information*-optimum state of Eq. (78) $\delta\boldsymbol{q}[p]$ replaces $\boldsymbol{q}[p]$, its resultant *gradient* information content [see Eq. (48)],

$$I[p,\Phi_{\boldsymbol{q}}] = I[p] + I[\Phi_{\boldsymbol{q}}] = I[p] + 4(\delta\boldsymbol{q})^2\int p(\boldsymbol{r})[\nabla\cdot\boldsymbol{f}(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r}, \tag{82}$$

exhibits the current contribution proportional to the squared deviation of the EO *wave*-number vector $\boldsymbol{q}$ from the configuration-average value $\langle\boldsymbol{q}\rangle$.

6 Atomic bases and orbitals reconstructing overlap distributions

The EO states $\{\varphi_{\boldsymbol{q}}(\mathrm{X}) \equiv \varphi_{\boldsymbol{q}}{}^{\mathrm{X}}(\boldsymbol{r})\}$ of constituent atoms X = A, B, … in a molecule,

$$\varphi^{\mathrm{X}}_{\boldsymbol{q}}(\boldsymbol{r}) = [p_{\mathrm{X}}(\boldsymbol{r})]^{1/2}\exp\{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{f}_{\mathrm{X}}[p_{\mathrm{X}};\boldsymbol{r}]\},\quad \langle\varphi_{\boldsymbol{q}}(\mathrm{X})|\varphi_{\boldsymbol{q}'}(\mathrm{X})\rangle = \delta(\boldsymbol{q}'-\boldsymbol{q}), \tag{83}$$

form an admissible (*non*-orthogonal) molecular basis for electronic structure calculations. They give rise to a non-vanishing (complex) diatomic (X ≠ Y) overlap integral,

$$\langle\varphi^{\mathrm{X}}_{\boldsymbol{q}}|\varphi^{\mathrm{Y}}_{\boldsymbol{q}'}\rangle = \int \mathrm{d}\boldsymbol{r}[p_{\mathrm{X}}(\boldsymbol{r})p_{\mathrm{Y}}(\boldsymbol{r})]^{1/2} \times\exp(i\{\boldsymbol{q}'\cdot\boldsymbol{f}_{\mathrm{Y}}[p_{\mathrm{Y}};\boldsymbol{r}]-\boldsymbol{q}\cdot\boldsymbol{f}_{\mathrm{X}}[p_{\mathrm{X}};\boldsymbol{r}]\}) \equiv \int \mathrm{d}\boldsymbol{r}\Omega_{\mathrm{X,Y}}(\boldsymbol{r})\exp[i\Phi_{\mathrm{X,Y}}(\boldsymbol{r})] \equiv O_{\boldsymbol{q},\boldsymbol{q}'}(\mathrm{X,Y}) = O_{\boldsymbol{q},\boldsymbol{q}'}(\mathrm{Y,X})^*, \tag{84}$$

the projection of $|\varphi^{\mathrm{Y}}_{\boldsymbol{q}'}\rangle$ on $|\varphi^{\mathrm{X}}_{\boldsymbol{q}}\rangle$ in the molecular Hilbert space, the element of the associated (Hermitian) EO-overlap matrix: $\mathbf{O} = \{O_{\boldsymbol{q},\boldsymbol{q}'}(\mathrm{X,Y})\} = \mathbf{O}^{\dagger}$.

Since the *complex* AO are characterized by their probability and current distributions, the natural question arises about the chemically favorable combinations of these physical descriptors of AIM subsystems in a molecule. In particular, one would like to address the intriguing question, how to combine the probability currents to facilitate/enhance the chemical bonds between AIM or reactant fragments? The *constructive* superposition of subsystem probabilities in the *bonding* MO combinations of the *real* AO and their *destructive* superposition pattern in the *antibonding* MO states have been well established in the familiar MO theory of molecular electronic structure. Hence, the favorable MO combination of the subsystem EO calls for their summation in the *probability*-bonding combination,

$$\psi^{b}_{\mathrm{XY}} = \varphi^{\mathrm{X}}_{\boldsymbol{q}} + \lambda\varphi^{\mathrm{Y}}_{\boldsymbol{q}'},\quad \lambda > 0, \tag{85}$$

while the EO difference,

$$\psi^{nb}_{\mathrm{XY}} = \varphi^{\mathrm{X}}_{\boldsymbol{q}} - \kappa\varphi^{\mathrm{Y}}_{\boldsymbol{q}'},\quad \kappa > 0, \tag{86}$$

should be associated with the *probability*-antibonding situation.

The phase/current factors of atomic EO dynamically influence a chemical character of the bonding MO combination describing a given X–Y bond. One recalls that directions of atomic currents in *standard* EO states, for $\phi = 0$, are determined by the orbital *wave*-number vectors: $\boldsymbol{q}_{\mathrm{X}} = \boldsymbol{q}$ and $\boldsymbol{q}_{\mathrm{Y}} = \boldsymbol{q}'$. Therefore, in the *probability*-bonding combination of Eq. (85), the *inward* orientation of EO currents, toward the bonding region between the nuclei,

$$\psi^{b}_{\mathrm{XY}}(\mathrm{in}) = \varphi^{\mathrm{X}}_{\boldsymbol{q}}(\rightarrow) + \lambda\varphi^{\mathrm{Y}}_{\boldsymbol{q}'}(\leftarrow), \tag{87}$$

should enhance the covalent bond X–Y, while the *outward* pattern of EO currents,

$$\psi^{b}_{\mathrm{XY}}(\mathrm{out}) = \varphi^{\mathrm{X}}_{\boldsymbol{q}}(\leftarrow) + \lambda\varphi^{\mathrm{Y}}_{\boldsymbol{q}'}(\rightarrow), \tag{88}$$

is expected to weaken this bond component. Therefore, the ("static") *probability*-bonding combination of Eq. (85) can assume both the ("dynamic") *current*-bonding and *current*-antibonding characters of Eqs. (87) and (88), respectively. In such EO combinations, the current pattern (the structure of "becoming") determines different *time* evolutions of the same initial (bonding) probability distribution (the structure of "being").

Similar *current*-bonding and *current*-antibonding combinations of the subsystem MO, e.g., substrates in chemical reactions, can be encountered in molecular interactions. Consider two interacting (parallel) benzene rings of reactants, perpendicular to "z" axis passing through their centers. In the *bonding* combination of complex MO exhibiting finite ring currents, the *conrotatory* matching of the latter should indeed result in an attraction between the magnetic moments associated with these substrate currents, while their *disrotatory* pattern should produce a magnetic repulsion.

One can also design the EO bases for the specified probability distributions of molecular fragments, e.g., substrates in a chemical reaction. This application should facilitate an orbital interpretation of molecular interactions. The HZM construction of antisymmetric states can be generalized to generate any probability distribution. In particular, one can design the orthonormal EO of N electrons which yields the prescribed diatomic *overlap* distribution [75],

$$p_{\mathrm{X,Y}}(\boldsymbol{r}) = \left[p_{\mathrm{X}}(\boldsymbol{r})p_{\mathrm{Y}}(\boldsymbol{r})\right]^{1/2} \equiv \Omega_{\mathrm{XY}}(\boldsymbol{r}), \tag{89}$$

which represents the geometrical average of atomic probability densities $\{p_{\mathrm{Z}}(\boldsymbol{r})\}$,

$$\begin{aligned}\psi^{\mathrm{X,Y}}_{\boldsymbol{q}}(\boldsymbol{r}) &= [\Omega_{\mathrm{XY}}(\boldsymbol{r})]^{1/2}\exp\{i[\boldsymbol{q}\cdot\boldsymbol{f}[\Omega_{\mathrm{XY}},\boldsymbol{r}]\}\\ &\equiv [\Omega_{\mathrm{XY}}(\boldsymbol{r})]^{1/2}\exp[i\boldsymbol{q}\times\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r})],\end{aligned} \tag{90}$$

and then construct Slater determinants from alternative selections of different N such orbitals.

Following the development of Sect. 3, this *overlap*-HZM construction transforms $\boldsymbol{r}$ into

$$\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r}) = \boldsymbol{f}[\Omega_{\mathrm{XY}},\boldsymbol{r}] = F^{\mathrm{XY}}_{x}\boldsymbol{i} + F^{\mathrm{XY}}_{y}\boldsymbol{j} + F^{\mathrm{XY}}_{z}\boldsymbol{k}, \tag{91}$$

with the associated Jacobian relation between volume elements:

$$\mathrm{d}\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r}) = (2\pi)^3\Omega_{\mathrm{XY}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \tag{92}$$

This can be effected through the *overlap*-dependent vector field $\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r}) = \boldsymbol{f}[\Omega_{\mathrm{XY}}, \boldsymbol{r}]$ of the EO *phase* component,

$$F^{\mathrm{XY}}_{x}(x,y,z) = 2\pi\frac{\int_{-\infty}^{x}\mathrm{d}x'\,\Omega_{\mathrm{XY}}(x',y,z)}{\int_{-\infty}^{\infty}\mathrm{d}x'\,\Omega_{\mathrm{XY}}(x',y,z)}, \tag{93a}$$

$$F^{\mathrm{XY}}_{y}(y,z) = 2\pi\frac{\int_{-\infty}^{y}\mathrm{d}y'\int_{-\infty}^{\infty}\mathrm{d}x'\,\Omega_{\mathrm{XY}}(x',y',z)}{\int_{-\infty}^{\infty}\mathrm{d}y'\int_{-\infty}^{\infty}\mathrm{d}x'\,\Omega_{\mathrm{XY}}(x',y',z)}, \tag{93b}$$

$$F^{\mathrm{XY}}_{z}(z) = \frac{2\pi}{N}\int_{-\infty}^{z}\mathrm{d}z'\int_{-\infty}^{\infty}\mathrm{d}y'\int_{-\infty}^{\infty}\mathrm{d}x'\,\Omega_{\mathrm{XY}}(x',y',z'). \tag{93c}$$

It gives the functional Jacobian determinant of Eq. (88):

$$\begin{aligned}\frac{\partial\boldsymbol{F}_{\mathrm{XY}}}{\partial\boldsymbol{r}} &= \begin{vmatrix} \frac{\partial F^{\mathrm{XY}}_{x}}{\partial x} & 0 & 0\\ \frac{\partial F^{\mathrm{XY}}_{x}}{\partial y} & \frac{\partial F^{\mathrm{XY}}_{y}}{\partial y} & 0\\ \frac{\partial F^{\mathrm{XY}}_{x}}{\partial z} & \frac{\partial F^{\mathrm{XY}}_{y}}{\partial z} & \frac{\partial F^{\mathrm{XY}}_{z}}{\partial z}\end{vmatrix}\\ &= \left(\frac{\partial F^{\mathrm{XY}}_{x}}{\partial x}\right)\left(\frac{\partial F^{\mathrm{XY}}_{y}}{\partial y}\right)\left(\frac{\partial F^{\mathrm{XY}}_{z}}{\partial z}\right)\\ &= (2\pi)^3\Omega_{\mathrm{XY}}(\boldsymbol{r}).\end{aligned} \tag{94}$$

Again, the diagonal derivatives of the preceding equation can be also interpreted as the associated *conditional* distributions:

$$\begin{aligned}\left(\frac{\partial F^{\mathrm{XY}}_{x}}{\partial x}\right) &= 2\pi\,\Omega_{\mathrm{XY}}(\boldsymbol{r})/\int_{-\infty}^{+\infty}\Omega_{\mathrm{XY}}(\boldsymbol{r})\,\mathrm{d}x\\ &= 2\pi\Omega_{\mathrm{XY}}(x,y,z)/\Omega_{\mathrm{XY}}(y,z) \equiv 2\pi\,\Omega_{\mathrm{XY}}(x|y,z),\\ \left(\frac{\partial F^{\mathrm{XY}}_{y}}{\partial y}\right) &= 2\pi\int_{-\infty}^{+\infty}\Omega_{\mathrm{XY}}(x,y,z)\,\mathrm{d}x/\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Omega_{\mathrm{XY}}(x,y,z)\,\mathrm{d}x\,\mathrm{d}y\\ &= 2\pi\left[\Omega_{\mathrm{XY}}(y,z)/\Omega_{\mathrm{XY}}(z)\right] \equiv 2\pi\,\Omega_{\mathrm{XY}}(y|z),\\ \left(\frac{\partial F^{\mathrm{XY}}_{z}}{\partial z}\right) &= 2\pi\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Omega_{\mathrm{XY}}(x,y,z)\,\mathrm{d}x\,\mathrm{d}y \equiv 2\pi\,\Omega_{\mathrm{XY}}(z).\end{aligned} \tag{95}$$

The orthonormality of such transformed EO conserving the given overlap distribution can be then demonstrated directly, following the substitution of Eq. (27):

$$\begin{aligned}\int_{-\infty}^{\infty}\psi^{\mathrm{XY}}_{\boldsymbol{q}'}(\boldsymbol{r})^{*}\psi^{\mathrm{XY}}_{\boldsymbol{q}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} &= \int_{-\infty}^{\infty}\mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r})}\,\Omega_{\mathrm{XY}}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\\ &= \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{F}_{\mathrm{XY}}(\boldsymbol{r})}\frac{\partial\boldsymbol{F}_{\mathrm{XY}}}{\partial\boldsymbol{r}}\mathrm{d}\boldsymbol{r}\\ &= \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}\mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{F}_{\mathrm{XY}}}\mathrm{d}\boldsymbol{F}_{\mathrm{XY}} = \delta(\boldsymbol{q}-\boldsymbol{q}').\end{aligned} \tag{96}$$

The standard HZM construction, reproducing the prescribed *molecular* probability density $p(\boldsymbol{r})$, can be thus considered as representing a special case of the above *overlap* development for the equal fragment distributions:

$$p_X(\boldsymbol{r}) = p_Y(\boldsymbol{r}) = \Omega_{XY}(\boldsymbol{r}) = p(\boldsymbol{r}). \tag{97}$$

The generalized approach, however, allows one to generate the orthonormal basis for any average distribution, e.g., that resulting from the overlap between atomic orbitals, AIM, reactants, etc. Such an EO framework can be thus focused on the valence region of the overlap between the specified pair of AIM, which is mostly responsible for the chemical bond formation between such subsystems. It can be better suited for a more compact, chemical interpretation of the bonding patterns generated by atomic electron distributions.

As an illustrative example, consider an overlap between two spherical-Gaussian densities $\{G_\alpha(A_\alpha, \boldsymbol{R}_\alpha)\}$ corresponding to subsystems $\alpha=(a, b)$ (see "Appendix 1"), centered in positions $\{\boldsymbol{R}_\alpha\}$,

$$\begin{aligned} &p_\alpha(\boldsymbol{r}) = (2A/\pi)^{3/2} \exp[-A_\alpha(\boldsymbol{r}-\boldsymbol{R}_\alpha)^2] \equiv G_\alpha(A_\alpha, \boldsymbol{R}_\alpha), \\ &p_a(\boldsymbol{r}) = G_a\big(A, \boldsymbol{R}_a\big) \quad \text{and} \quad p_b(\boldsymbol{r}) = G_b\big(B, \boldsymbol{R}_b\big). \end{aligned} \tag{98}$$

Their product can be transformed into an effective Gaussian function

$$\begin{aligned} &p_a(\boldsymbol{r})p_b(\boldsymbol{r}) \propto \exp[-A(\boldsymbol{r}-\boldsymbol{R}_a)^2] \exp\big[-B(\boldsymbol{r}-\mathbf{R}_b)^2\big] \\ &= \exp\{-\big[AB/(A+B)\big](\boldsymbol{R}_a-\boldsymbol{R}_b)^2\} \exp[-(A+B)(\boldsymbol{r}-\boldsymbol{\rho}_{ab})^2], \end{aligned} \tag{99}$$

where $\boldsymbol{\rho}_{ab}=(A\boldsymbol{R}_a+B\boldsymbol{R}_b)/(A+B)$. It also generates the Gaussian *average* density,

$$\begin{aligned} \Omega_{ab}(\boldsymbol{r}) &= \big[p_a(\boldsymbol{r})p_b(\boldsymbol{r})\big]^{1/2} \\ &= (2/\pi)^{3/2}(AB)^{3/4} \exp\{-(AB/[2(A+B)])(\boldsymbol{R}_a-\boldsymbol{R}_b)^2\} \\ &\quad \times \exp\{-\big[(A+B)/2\big](\boldsymbol{r}-\boldsymbol{\rho}_{ab})^2\}, \end{aligned} \tag{100}$$

which provides the distribution basis of the associated *overlap* EO of Eq. (90). As shown in "Appendix 1," the HZM conditional probabilities and local *phase*-vector components for such an effective spherical-Gaussian distribution are readily available.

7 Conclusion

In this article, we have first summarized the probability and phase continuities of molecular states, as implied be SE. We have then reexamined the HZM construction of DFT, of antisymmetric states yielding the prescribed electron density, and provided the probability interpretation of its key *phase* concept. It has been argued that this transformed *position* representation in fact preserves main features of the *momentum* representation in molecular quantum mechanics. A need for the quantum extension of the familiar *classical* (probability) measures of the entropy/information content in molecular states, to accommodate the complex wave functions of the quantum–mechanical description, has been stressed, and *resultant* descriptors combining the probability and phase/current contributions have been introduced. This quantum generalization of Fisher's *gradient* information, related to electronic kinetic energy, generates a nonvanishing *information* source. We have also demonstrated the nonclassical (current) origins of the associated *resultant*-information production. The present analysis and related treatments of reactivity phenomena [23–28] complement the previous classical information approaches to reactive systems, e.g., [82–86].

The orbital flows of electrons have been examined, and the *information*-optimum "thermodynamic" phases of the *information*-equilibrium EO states have been determined. It has been argued that the overall current of electron configurations in such *information* equilibria identically vanishes. The current orientations in the bonding combinations of atomic EO have been examined and the *current*-bonding or *current*-antibonding patterns have been identified. Finally, the EO basis reproducing the specified diatomic *overlap* density has been discussed and an illustrative example of the overlapping Gaussian distributions has been explored.

This article further develops the resultant-information description of molecular states [26–28, 86]. The electronic state exhibiting a nonvanishing probability current indeed contains more information, compared to the zero-current state of the same electron density, since the former exhibits an additional structural element, and thus also the associated coherence information of the phase/flux pattern, which is missing in the state specification by the probability distribution alone. Following Prigogine [29], one could refer at this point to the now famous picture of a complicated network of vortices on Jupiter. The current structure of "becoming" contains the information about the (subsequent) quantum evolution of the system temporary probability distribution, the structure of "being," thus representing the state of a greater "knowledge" about the system, as reflected by the higher degree of the gradient "order" (determinicity) information, corresponding to lower level of the system "uncertainty," corresponding to smaller gradient "disorder" (indeterminicity) information (entropy) measure.

Appendix 1: HZM construction for the *spherical*-Gaussian probability distribution

Consider the 1*s*-type spherical-Gaussian orbital (SGO) centered at the origin ($\boldsymbol{R}=\boldsymbol{0}$) of the Cartesian coordinate system $\{x_\alpha\}$,

$$s_\mu(\boldsymbol{r}) = G(\mu,\boldsymbol{R}) = (2\mu/\pi)^{3/4}\exp[-\mu(\boldsymbol{r}-\boldsymbol{R})^2], \left\langle s_\mu \middle| s_\mu \right\rangle = 1, \tag{A1}$$

and the probability density it generates,

$$\begin{aligned} p_\mu(\boldsymbol{r}) = s_\mu(\boldsymbol{r})^2 &= (2\mu/\pi)^{3/2}\exp(-2\mu\boldsymbol{r}^2) \\ &= \left[(2\mu/\pi)^{1/2}\exp(-2\mu x^2)\right]\left[(2\mu/\pi)^{1/2}\exp(-2\mu y^2)\right] \\ &\quad\times\left[(2\mu/\pi)^{1/2}\exp(-2\mu z^2)\right] \\ &\equiv p_\mu(x)p_\mu(y)p_\mu(z), \quad \int p_\mu(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = 1, \end{aligned} \tag{A2}$$

expressed in terms of the coordinate distributions

$$\{p_\mu(x_\alpha)\}, \quad \int p_\mu(x_\alpha)\mathrm{d}x_\alpha = 1, \quad x_\alpha = x,y,z. \tag{A3}$$

The factorization of Eq. (A2) and partial normalization of Eq. (A3) then imply the following joint and conditional probability distributions:

$$\begin{aligned} &p_\mu(x,y,z) = p_\mu(\boldsymbol{r}) = p_\mu(x)p_\mu(y)p_\mu(z), \\ &p_\mu(y,z) = p_\mu(y)p_\mu(z), \quad p_\mu(y|z) = p_\mu(y), \quad p_\mu(x|y,z) = p_\mu(x). \end{aligned} \tag{A4}$$

Following the HZM prescription, the corresponding components of the local *phase* vector $\boldsymbol{f}_\mu[p;\boldsymbol{r}] \equiv \boldsymbol{f}_\mu(\boldsymbol{r}) = \{f_{\mu,\alpha}(\boldsymbol{r})\}$ are defined by the partial integrals of Eq. (23). One first observes that the construction definite integrals read:

$$\begin{aligned} &\int p_\mu(x',y,z)\mathrm{d}x' = p_\mu(y)p_\mu(z)\int p_\mu(x')\mathrm{d}x' = p_\mu(y)p_\mu(z) \text{ and} \\ &\iint p_\mu(x',y',z)\mathrm{d}x'\mathrm{d}y' = p_\mu(z)\left[\int p_\mu(x')\mathrm{d}x\right]\left[\int p_\mu(x')\mathrm{d}x'\right] = p_\mu(z). \end{aligned} \tag{A5}$$

Its indefinite integrals can be thus expressed in terms of the familiar error function of probability theory,

$$\mathrm{erf}(s) = [2/\sqrt{\pi}]\int_0^s \exp(-t^2)\,\mathrm{d}t, \tag{A6}$$

$$\int_{-\infty}^{x_\alpha} p_\mu(x_\alpha')\,\mathrm{d}x_\alpha' = \frac{1}{2}[1+\mathrm{erf}(x_\alpha)]. \tag{A7}$$

The resulting components of the *phase* vector for this spherical-Gaussian probability density thus read:

$$f_{\mu,\alpha}(\boldsymbol{r}) = \pi[1+\mathrm{erf}(x_\alpha)] = f_{\mu,\alpha}(x_\alpha). \tag{A8}$$

Finally, by direct differentiation one can verify Eq. (25) which determines the construction Jacobian of Eq. (24).

Appendix 2: Thermodynamic phase from extremum principle for nonclassical information

Consider first the resultant-information content [Eq. (45)] in the single original (nontransformed) EO of Eq. (17), for $\phi=0$,

$$\psi_{\boldsymbol{q}}(\boldsymbol{r}) = [p(\boldsymbol{r})]^{1/2}\exp[i\boldsymbol{q}\cdot\boldsymbol{f}(\boldsymbol{r})] \equiv [p(\boldsymbol{r})]^{1/2}\exp[iF_{\boldsymbol{q}}(\boldsymbol{r})], \tag{B1}$$

$$\begin{aligned} I[\psi_{\boldsymbol{q}}[p]] &= \langle\psi_{\boldsymbol{q}}[p]|\hat{\mathrm{I}}|\psi_{\boldsymbol{q}}[p]\rangle = 4\langle\nabla\psi_{\boldsymbol{q}}[p]|\nabla\psi_{\boldsymbol{q}}[p]\rangle \\ &= I[p] + 4\int p(\boldsymbol{r})\left[\nabla F_{\boldsymbol{q}}(\boldsymbol{r})\right]^2\mathrm{d}\boldsymbol{r} \\ &= I[p] + 4\boldsymbol{q}^2\int p(\boldsymbol{r})[\nabla\cdot\boldsymbol{f}(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \equiv I[p] + I[\boldsymbol{q}[p],\boldsymbol{f}[p]]. \end{aligned} \tag{B2}$$

This classical information term is thus uniquely determined by the electron probability distribution $p(\boldsymbol{r})$. Indeed, both $\boldsymbol{q}$ and $\boldsymbol{f}$ are unique functionals of p: the former—by the energy—minimum principle of quantum mechanics, and the latter—by the HZM construction.

After the *thermodynamic*-phase transformation,

$$\varphi_{\boldsymbol{q}}(\boldsymbol{r}) = \psi_{\mathbf{q}}(\boldsymbol{r})\,\exp[\mathrm{i}\phi(\boldsymbol{r})], \tag{B3}$$

the overall classical information content in such an *information*-equilibrium state is supplemented by ϕ-dependent, nonclassical contributions:

$$\begin{aligned} I[\varphi_{\boldsymbol{q}}] &= \left\langle\varphi_{\boldsymbol{q}}\middle|\hat{\mathrm{I}}\middle|\varphi_{\boldsymbol{q}}\right\rangle = 4\left\langle\nabla\varphi_{\boldsymbol{q}}|\nabla\varphi_{\boldsymbol{q}}\right\rangle \\ &= I[\psi_{\boldsymbol{q}}[p]] + 4\int p(\boldsymbol{r})[\nabla\phi(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \\ &\quad - 4i\int[\nabla\phi(\boldsymbol{r})]\cdot[\psi_{\boldsymbol{q}}(\boldsymbol{r})^*\nabla\psi_{\boldsymbol{q}}(\boldsymbol{r}) - \psi_{\boldsymbol{q}}(\boldsymbol{r})\nabla\psi_{\boldsymbol{q}}(\boldsymbol{r})^*]\mathrm{d}\boldsymbol{r} \\ &= I[\psi_{\boldsymbol{q}}[p]] + 4\int p(\boldsymbol{r})[\nabla\phi(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \\ &\quad - 4i\int[\nabla\phi(\boldsymbol{r})]\cdot(2mi/\hbar)\boldsymbol{j}_{\boldsymbol{q}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &= I[\psi_{\boldsymbol{q}}[p]] + 4\int p(\boldsymbol{r})[\nabla\phi(\boldsymbol{r})]^2\mathrm{d}\boldsymbol{r} \\ &\quad + 8\boldsymbol{q}\int p(\boldsymbol{r})\nabla\phi(\boldsymbol{r})\nabla\cdot\boldsymbol{f}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &= I[\psi_{\boldsymbol{q}}[p]] + I[\phi] + I[\boldsymbol{f},\phi]. \end{aligned} \tag{B4}$$

The *information*-equilibrium *thermodynamic* phase, for the fixed probability distribution, then results from the extremum of the nonclassical information contribution,

$$\delta(I[\phi] + I[\boldsymbol{f}, \phi])/\delta\phi(\boldsymbol{r})|_{\text{opt.}} = 0, \tag{B5}$$

which gives the following Euler's equation for the *information*-optimum phase of EO:

$$\begin{aligned}\nabla\{\boldsymbol{q}p(\boldsymbol{r})\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + p(\boldsymbol{r})\nabla\phi_{\text{opt.}}(\boldsymbol{r})\}\\ = \nabla p(\boldsymbol{r})\cdot\{\boldsymbol{q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) + \nabla\phi_{\text{opt.}}(\boldsymbol{r})\} = 0,\end{aligned} \tag{B6}$$

where we have recognized the *phase* continuities of Eq. (11): $\nabla^2 F_{\boldsymbol{q}} = \nabla^2\phi_{\text{opt.}} = 0$. It thus follows from the preceding equation that

$$\nabla\phi_{\text{opt.}}(r) = -\boldsymbol{q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r}). \tag{B7}$$

Finally, for the specified configuration of N electrons [Eq. (28)], identified by the set of the occupied *information*-equilibrium EO $\{\varphi_l^{opt.}\}$, one finds by summation over the orbital relations (B7),

$$\begin{aligned}&\sum_l[\nabla\phi_{\text{opt.}}(\boldsymbol{r})] = N\nabla\phi_{\text{opt.}}(\boldsymbol{r}) = -(\sum_l \boldsymbol{q}_l)\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) = -\boldsymbol{Q}\nabla\cdot\boldsymbol{f}(\boldsymbol{r}) \text{ or}\\ &\nabla\phi_{\text{opt.}}(\boldsymbol{r}) = -\langle\boldsymbol{q}\rangle\nabla\cdot\boldsymbol{f}(r),\end{aligned} \tag{B8}$$

and hence [see Eq. (76)]:

$$\phi_{\text{opt.}}(\boldsymbol{r}) = -\langle\boldsymbol{q}\rangle\boldsymbol{f}(\boldsymbol{r}) + \text{const.} \equiv -\langle\boldsymbol{q}\rangle\boldsymbol{f}(\boldsymbol{r}). \tag{B9}$$

References

1. Fisher RA (1925) Theory of statistical estimation. Proc Camb Philos Soc 22:700–725
2. Frieden BR (2004) Physics from the Fisher information—a unification. Cambridge University Press, Cambridge
3. Shannon CE (1948) The mathematical theory of communication. Bell System Tech J 27(379–493):623–656
4. Shannon CE, Weaver W (1949) The mathematical theory of communication. University of Illinois, Urbana
5. Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. Phys Rev 136B:864–971
6. Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. Phys Rev 140A:133–1138
7. Levy M (1979) Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the *v*-representability problem. Proc Natl Acad Sci USA 76:6062–6065
8. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, New York
9. Dreizler RM, Gross EKU (1990) Density functional theory: an approach to the quantum many-body problem. Springer, Berlin
10. Nalewajski RF (ed) (1996) Density functional theory I–IV, topics in current chemistry vol 180–183
11. Nalewajski RF (2016) Complex entropy and resultant information measures. J Math Chem 54:1777–1782
12. Nalewajski RF (2014) On phase/current components of entropy/information descriptors of molecular states. Mol Phys 112:2587–2601
13. Nalewajski RF (2017) Quantum information measures and their use in chemistry. Curr Phys Chem 7:94–117
14. Nalewajski RF (2013) Exploring molecular equilibria using quantum information measures. Ann Phys (Leipzig) 525:256–268
15. Nalewajski RF (2016) Quantum information theory of molecular states. Nova Science Publishers, New York
16. Nalewajski RF (2014) On phase equilibria in molecules. J Math Chem 52:588–612
17. Nalewajski RF (2014) Quantum information approach to electronic equilibria: molecular fragments and elements of non-equilibrium thermodynamic description. J Math Chem 52:1921–1948
18. Nalewajski RF (2015) Phase/current information descriptors and equilibrium states in molecules. Int J Quantum Chem 115:1274–1288
19. Nalewajski RF (2015) Quantum information measures and molecular phase equilibria. In: Baswell AR (ed) Advances in mathematics research, vol 2. Nova Science Publishers, New York, pp 53–86
20. Nalewajski RF (2018) Information equilibria, subsystem entanglement and dynamics of overall entropic descriptors of molecular electronic structure. J Mol Model (Chattaraj PK issue) 24:212–227
21. Nalewajski RF (2017) Entropy continuity, electron diffusion and fragment entanglement in equilibrium states. In: Baswell AR (ed) Advances in mathematics research, vol 22. Nova Science Publishers, New York, pp 1–42
22. Nalewajski RF (2016) On entangled states of molecular fragments. Trends Phys Chem 16:71–85
23. Nalewajski RF (2018) Phase description of reactive systems. In: Islam N, Kaya S (eds) Conceptual density functional theory. Apple Academic Press, Waretown, pp 217–249
24. Nalewajski RF (2017) Chemical reactivity description in density-functional and information theories. Acta Phys Chim Sin 33:2491–2509
25. Nalewajski RF (2019) On entropy/information description of reactivity phenomena. In: Baswell AR (ed) Advances in mathematics research, vol 26. Nova Science Publishers, New York
26. Nalewajski RF (2019) Quantum information perspective on chemical reactivity. In: Islam N (ed) Recent trends in theoretical and computational research (in press)
27. Nalewajski RF (2019) Role of electronic kinetic energy and resultant gradient information in chemical reactivity. In: Berski S, Sokalski WA (eds) J Mol Model (Latajka Z issue) (in press)
28. Nalewajski RF (2019) Understanding electronic structure and chemical reactivity: quantum-information perspective. Appl Sci 9:1262–1292
29. Prigogine I (1980) From being to becoming: time and complexity in the physical sciences. Freeman WH & Co, San Francisco
30. Kullback S, Leibler RA (1951) On information and sufficiency. Ann Math Stat 22:79–86
31. Kullback S (1959) Information theory and statistics. Wiley, New York
32. Abramson N (1963) Information theory and coding. McGraw-Hill, New York
33. Pfeifer PE (1978) Concepts of probability theory. Dover, New York
34. Nalewajski RF (2006) Information theory of molecular systems. Elsevier, Amsterdam
35. Nalewajski RF (2010) Information origins of the chemical bond. Nova Science Publishers, New York
36. Nalewajski RF (2003) Electronic structure and chemical reactivity: density functional and information theoretic perspectives. Adv Quant Chem 43:119–184
37. Nalewajski RF (2012) Perspectives in electronic structure theory. Springer, Heidelberg
38. Nalewajski RF, Parr RG (2000) Information theory, atoms-in-molecules and molecular similarity. Proc Natl Acad Sci USA 97:8879–8882

39. Nalewajski RF (2003) Information principles in the theory of electronic structure. Chem Phys Lett 372:28–34
40. Nalewajski RF (2003) Information principles in the Loge theory. Chem Phys Lett 375:196–203
41. Nalewajski RF, Broniatowska E (2003) Information distance approach to Hammond postulate. Chem Phys Lett 376:33–39
42. Nalewajski RF, Parr RG (2001) Information theory thermodynamics of molecules and their Hirshfeld fragments. J Phys Chem A 105:7391–7400
43. Nalewajski RF (2002) Hirshfeld analysis of molecular densities: subsystem probabilities and charge sensitivities. Phys Chem Chem Phys 4:1710–1721
44. Parr RG, Ayers PW, Nalewajski RF (2005) What is an atom in a molecule? J Phys Chem A 109:3957–3959
45. Nalewajski RF, Broniatowska E (2007) Atoms-in-molecules from the stockholder partition of molecular two-electron distribution. Theor Chem Acc 117:7–27
46. Heidar-Zadeh F, Ayers PW, Verstraelen T, Vinogradov I, Vöhringer-Martinez E, Bultinck P (2018) Information-theoretic approaches to atoms-in-molecules: Hirshfeld family of partitioning schemes. J Phys Chem A 122:4219–4245
47. Hirshfeld FL (1977) Bonded-atom fragments for describing molecular charge densities. Theor Chim Acta (Berl) 44:129–138
48. Nalewajski RF (2000) Entropic measures of bond multiplicity from the information theory. J Phys Chem A 104:11940–11951
49. Nalewajski RF (2004) Entropy descriptors of the chemical bond in Information Theory: I. Basic concepts and relations. Mol Phys 102:531–546; II. Application to simple orbital models. Mol Phys 102:547–566
50. Nalewajski RF (2004) Entropic and difference bond multiplicities from the two-electron probabilities in orbital resolution. Chem Phys Lett 386:265–271
51. Nalewajski RF (2005) Reduced communication channels of molecular fragments and their entropy/information bond indices. Theor Chem Acc 114:4–18
52. Nalewajski RF (2005) Partial communication channels of molecular fragments and their entropy/information indices. Mol Phys 103:451–470
53. Nalewajski RF (2011) Entropy/information descriptors of the chemical bond revisited. J Math Chem 49:2308–2329
54. Nalewajski RF (2014) Quantum information descriptors and communications in molecules. J Math Chem 52:1292–1323
55. Nalewajski RF (2009) Multiple, localized and delocalized/conjugated bonds in the orbital-communication theory of molecular systems. Adv Quant Chem 56:217–250
56. Nalewajski RF, Szczepanik D, Mrozek J (2011) Bond differentiation and orbital decoupling in the orbital communication theory of the chemical bond. Adv Quant Chem 61:1–48
57. Nalewajski RF, Szczepanik D, Mrozek J (2012) Basis set dependence of molecular information channels and their entropic bond descriptors. J Math Chem 50:1437–1457
58. Nalewajski RF (2017) Electron communications and chemical bonds. In: Wójcik M, Nakatsuji H, Kirtman B, Ozaki Y (eds) Frontiers of quantum chemistry. Springer, Singapore, pp 315–351
59. Nalewajski RF, Świtka E, Michalak A (2002) Information distance analysis of molecular electron densities. Int J Quantum Chem 87:198–213
60. Nalewajski RF, Broniatowska E (2003) Entropy displacement analysis of electron distributions in molecules and their Hirshfeld atoms. J Phys Chem A 107:6270–6280
61. Nalewajski RF (2008) Use of Fisher information in quantum chemistry. Int J Quantum Chem (Jankowski K issue) 108:2230–2252
62. Nalewajski RF, Köster AM, Escalante S (2005) Electron localization function as information measure. J Phys Chem A 109:10038–10043
63. Becke AD, Edgecombe KE (1990) A simple measure of electron localization in atomic and molecular systems. J Chem Phys 92:5397–5403
64. Silvi B, Savin A (1994) Classification of chemical bonds based on topological analysis of electron localization functions. Nature 371:683–686
65. Savin A, Nesper R, Wengert S, Fässler TF (1997) ELF: the electron localization function. Angew Chem Int Ed Engl 36:1808–1832
66. Nalewajski RF, de Silva P, Mrozek J (2010) Use of nonadditive Fisher information in probing the chemical bonds. J Mol Struct: Theochem 954:57–74
67. Nalewajski RF (2011) Through-space and through-bridge components of chemical bonds. J Math Chem 49:371–392
68. Nalewajski RF (2011) Chemical bonds from through-bridge orbital communications in prototype molecular systems. J Math Chem 49:546–561
69. Nalewajski RF (2011) On interference of orbital communications in molecular systems. J Math Chem 49:806–815
70. Nalewajski RF, Gurdek P (2011) On the implicit bond-dependency origins of bridge interactions. J Math Chem 49:1226–1237
71. Nalewajski RF (2012) Direct (through-space) and indirect (through-bridge) components of molecular bond multiplicities. Int J Quantum Chem 112:2355–2370
72. Nalewajski RF, Gurdek P (2012) Bond-order and entropic probes of the chemical bonds. Struct Chem 23:1383–1398
73. Harriman JE (1980) Orthonormal orbitals for the representation of an arbitrary density. Phys Rev A 24:680–682
74. Zumbach G, Maschke K (1983) New approach to the calculation of density functionals. Phys Rev A28: 544–554; Erratum, Phys. Rev. A29: 1585–1587
75. Nalewajski RF (2000) Orthonormal orbitals from the overlapping densities of subsystems. J Mol Struct (Theochem) 501:529–534
76. Callen HB (1962) Thermodynamics: an introduction to the physical theories of equilibrium thermostatics and irreversible thermodynamics. Wiley, New York
77. Macke W (1955) Zur wellermechanischen behandlung von vielkoeperproblemen. Ann Phys 17:1–9
78. Macke W (1955) Wave mechanical treatment of the Fermi gas. Phys Rev 100:992–993
79. Gilbert TL (1975) Hohenberg–Kohn theorem for nonlocal external potentials. Phys Rev B 12:2111–2120
80. Sears SB, Parr RG, Dinur U (1980) On the quantum mechanical kinetic energy as a measure of the information in a distribution. Isr J Chem 19:165–173
81. von Weizsäcker CF (1935) Zur theorie der kernmassen. Z Phys 96:431–458
82. Hô M, Schmider HL, Weaver DF, Smith VH Jr, Sagar RP, Esquivel RO (2000) Shannon entropy of chemical changes: S_N2 displacement reactions. Int J Quantum Chem 77:376–382
83. López-Rosa S, Esquivel RO, Angulo JC, Antolin J, Dehesa JS, Flores-Gallegos N (2010) Fisher information study in position and momentum spaces for elementary chemical reactions. J Chem Theory Comput 6:145–154
84. Esquivel RO, Liu SB, Angulo JC, Dehesa JS, Antolin J, Molina-Espiritu M (2011) Fisher information and steric effect: study of the internal rotation barrier in ethane. J Phys Chem A115:4406–4415
85. Liu SB (2016) Information-theoretic approach in density-functional reactivity theory. Acta Phys Chim Sin 32:98–118
86. Nalewajski RF (2019) Resultant information description of electronic states and chemical processes. J Phys Chem A (Geerlings P issue) (submitted)